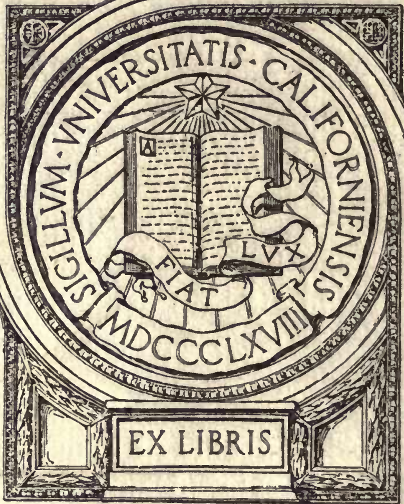
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LECTURE-NOTES

ON

THEORETICAL CHEMISTRY.

BY

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To

My Parents,

In Gratitude.

PREFACE.

The study of theoretical chemistry has not, in general, met with that recognition and appreciation which is warranted by the interest and importance attaching to this branch of chemical science.

Seeking for an explanation, it appears that to many this study presents considerable difficulty, on account of the number and variety of themes—frequently exhibiting no organic connection—to which the attention of the student is invited.

The difficulty is inherent in the nature of the subject, for as yet there is no philosophy of chemistry, and work in this domain, of necessity resolves itself into a study of the material from which such a philosophy may, at some future time, be constructed.

May these pages be of service to those who are entering upon a study of these subjects.

It has been the intention of the writer to offer a general view over the wide domain of chemical theory, to exhibit, as clearly as might be, the correlation of the many lines of research along which investigations of the questions of theoretical chemistry are at present conducted, and, last but not least, to point out the practical bearing of its teachings on problems to be constantly met with in the application of chemical knowledge.

As indicated by its title, this treatise does not pretend to offer an exhaustive discussion of the subjects considered; volumes have been written on most of the topics to which here but a scant chapter or two has been devoted. Indeed, it is one of the aims of this book to incite to a thorough study of this literature, a literature so constantly increasing in scope and in importance.

With this object in view, a list of works on theoretical chemistry is placed at the end of this volume. This list is believed to be sufficiently comprehensive to meet the requirements of most students. To facilitate the study of the subject from an historical point of view, the titles given are arranged in chronological order.

The periodicals enumerated, barring some few exceptions, of course devote but a part of their space to papers of the character here considered, yet reference to them has been deemed expedient, because frequently important researches are first recorded in their columns.

Considerable prominence has been given in these pages to stoichiometry—the arithmetic of chemistry—and examples are freely introduced in illustration of the different principles discussed.

A thorough working familiarity with these principles of stoichiometry is essential, and should be acquired by the solving of numerous problems; however, insertion of such problems seemed superfluous, in view of the fact that several excellent collections of this kind have been but recently published.

In making acknowledgment of his obligations, the writer would state that he has considered it his duty, no less than his pleasure, to consult all sources of information available.

No attempt has been made to cite and to give credit for individual articles referred to in the journal literature; however, the periodicals in which they appear are named.

All books consulted, are marked by asterisks in the bibliography appended, but special mention must be made of the writer's indebtedness to the standard works of Kopp, Ostwald, and Muir.

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LECTURE-NOTES
ON
THEORETICAL CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

KNOWLEDGE consists in an intelligent perception and understanding of facts and ideas.

Science is systematized knowledge.

A science which has been established solely by the process of reasoning, which deduces theories from ideas, which does not base on experience, is termed a deductive science; the pure mathematics will serve as an illustration of this type.

A science which rests on observation and experience, which owes its existence to the inference of theories and the evolution of laws from observed facts, is an inductive science; chemistry is a representative science of this character.

The aims pursued by the devotees of chemistry have at various times been so very different, that chemistry, in the sense in which the term is now understood, is a science of comparatively recent origin.

The very beginning of chemical history can be traced back to the remote past. However, until the fourth century no attempt was made to collate the chemical facts then known, or to employ them for the attainment of any definite purpose.

The era beginning with the fourth century and extending to the first quarter of the sixteenth century may be denoted as the age of alchemy. From that time on, and to the middle of the seventeenth century, chemistry was made to serve the interests of medicine, and this period is designated as the age of medical chemistry or iatro-chemistry. It was with the termination of this era that chemistry entered upon the pursuit of independent and well-defined aims.

Origin and Meaning of the Term Chemistry.—The origin of the word chemistry is involved in some doubt. The first one to record this expression was, it seems, Julius Maternus Firmicus, who lived about 340 A.D.

This author wrote a treatise on astronomy entitled "Mathesis." Among other matters there is in this work a reference to the influence exercised on the inclinations of mortal man by the relative position which the moon and a planet may chance to hold at the hour of his birth. In this instance the word "Alchemiæ," or, as some manuscripts have it, "Chemiæ," is used for the first time in a sense similar to that in which the expression chemical knowledge is used at the present time. This author, however, gives no explanation or definition of the term, apparently assuming the word "Chemia" to be well known.

The true meaning of the word chemistry has also been a matter of considerable doubt. Two appellations, "Chemia" and "Chymia," have been in use for a long time, and these terms admit of different interpretations as to their origin. Of these two expressions the term "Chemia" is the older, "Chymia" being of a more recent date.

It is most probable that the first attempt to collate chemical facts and to apply them to the solving of any one task, was made in Egypt. It is also likely that the art which was the result of this attempt, was named from the country where it originated.

According to Plutarch, about 100 A.D., the original name of Egypt was *Χημία*, Chemia. This name was given to it on account of the black color of its soil. The black of the eye, the pupil, as the symbol of the dark and mysterious, was also denoted by the same term. It seems, therefore, most probable that the word chemistry originally meant Egyptian knowledge, and later on, it was frequently termed the secret, or the black art.

Zosimus, about 400 A.D., used the term *χημίᾶ* to indicate the whole of the secret art which was said to have been imparted to man by superior beings, and in which the art of making gold and silver was included.

In later times the expression "Chymia" was assigned to all knowledge of this description, and the use of this term has led to an attempt to account in a different way for the name of this science. It is said to have been derived from the Greek word *χυμός*, a fluid or sap, and it was inferred that thereby the art to work with solutions was indicated. This word has the same root as the Greek word *χέω*, to pour out, to make fluid, to melt; yet for various reasons the above inference concerning the origin of the word chemistry, seems untenable.

Aims of Chemistry and of Chemical Philosophy.—The aim of chemistry is the study of matter—the constitution of matter, its properties and its transformations. This indicates at once the wide range and scope of this branch of knowledge.

In order to facilitate the work and to permit of a comprehensive view over the whole field, a division of the subject into various sections has been made, as, for instance, into general chemistry, applied chemistry, analytical chemistry. But whatever the classification into groups or sections, the task of chemical philosophy is to generalize all information gained in the study and in the laboratory, to seek out the relation between chemical phenomena and their causes, to trace the laws which govern these phenomena, and ultimately, by the comparison and co-ordination of numerous data secured by observation and experiment, to deduce and establish the fundamental principles of chemical science.

Chemistry, as a philosophical system, is as yet in the period of evolution, and probably is still far from the form in which it will ultimately rest.

Newly-discovered facts call for explanation; new hypotheses are constantly appearing; new theories displace the old. As, however, in the development of all sciences, so in chemistry, no advance can ever displace a truth once discovered and established, although the form in which it is expressed, may have to be greatly modified or extended.

It is important to assign their proper value to inferences and conclusions which may be drawn from observations, and care should be taken to employ correctly the terms hypothesis, theory, and law.

An *hypothesis* is a supposition provisionally adopted to account for and to explain certain facts; it is a tentative conjecture concerning the nature and cause of phenomena.

A *theory* represents the logical deductions that can be drawn from a working hypothesis; it is an exposition of general principles, and is intended to exhibit the relations existing between the parts of a systematic whole.

The crucial test as to the value and validity of any hypothesis or theory rests of course in its concordance with the facts ascertained by experiment and observation.

The discovery and establishment of any fact or facts which may not be in harmony with a given hypothesis or theory, of course forces the abandonment, or at least the modification, of the latter, and calls for the formulation of some theory which shall take due account of such newly-ascertained facts.

A *law* may be defined as a mode or order of sequence. A law must not only embrace all known facts and phenomena to which it refers, but it must also be able to account for all. phenomena of like character which may ever be discovered

In fact, a law must, to a certain extent, be capable of predicting the existence of such phenomena.

Definitions.—There are a few terms used in chemical science which are also frequently employed in general language. As a clear conception of the precise meaning assigned in science to these terms is essential, the following definitions may not be superfluous:

Matter. That which has extension, which occupies space; which is perceptible by the senses; which constitutes the universe.

Mass. Any portion of matter appreciable by the senses. Also, the amount (quantity) of matter in a substance.

Molecule. The smallest particle into which matter can be divided without destroying its identity.

Atom. The smallest quantity of matter that can enter into chemical combination.

Weight. The amount of attraction between two masses; in a restricted sense, the amount of attraction of the earth on a substance.

Volume. The amount of space occupied by a substance.

Motion. Change of position.

Rest. Permanence of position.

Work. The overcoming of resistance.

Energy. The power of doing work; the cause of all change experienced by matter.

Force. Included in above definition of energy; in a more restricted sense, any cause which tends to produce, change, or destroy motion.

Stoichiometry.—The term stoichiometry is derived from the Greek *στοιχεῖον*, elementary substance, and *μέτρον*, measure. It treats of the quantitative relations of chemical substances.

The idea that salts contain acid and alkali in definite proportions, seems to have been held at a very early date; at least, certain passages in the writings of Geber, an alchemist of the eighth century, are quoted in support of this view, Definite evidence of it is certainly found in the writings of Van Helmont, 1640, and in 1699 Homberg made an investigation in order to ascertain the quantities of different acids which would combine with a stated amount of alkali.

The outlines of stoichiometrical teachings, to the extent to which they had been developed up to that time, were published by a German, Carl Friedrich Wenzel, in 1777.*

The term stoichiometry was introduced by another German chemist, Jeremias Benjamin Richter, most of whose writings treat of the application of mathematics to chemistry. In 1792–94 this author published a work of three volumes relating to stoichiometry.†

The growth of this branch of chemistry was by no means rapid. The law of combination in definite proportions was first enunciated by Proust in 1801, with reference to oxides. The law of multiple proportions was discovered by Dalton. Dalton's views, which he had conceived as early as 1804, were published only in 1807 in Thomson's "System of Chemistry." In the year following, Dalton issued his own work, "New System of Chemical Philosophy," in which his views and teachings were fully stated.

Active among the workers who advanced theoretical chemistry in the latter part of the eighteenth, and in the earlier part of this century, were Lavoisier, Gay-Lussac, Von Humboldt, Berzelius, and Avogadro.

At the present time, chemistry is rapidly approaching the condition of an exact science, and in consequence, the study of stoichiometry is one of growing importance; even now it would seem, that the day is not far distant when chemistry shall become firmly established on a mathematical basis.

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* Vorlesungen über die chemische Verwandtschaft der Körper.

† Stöchiometrie oder Messkunst chymischer Elemente.

CHAPTER II.

SPECIFIC GRAVITY.

Definition of Specific Gravity.—The specific gravity of a substance is the ratio of its mass to the mass of an equal volume of some other substance taken as unity.

Standards of Specific Gravity.—The choice of standards of specific gravity has been an arbitrary one. For solid and for liquid substances the standard now universally adopted, is pure water at its greatest density, that is, at 4° C.

The standard selected for gases and vapors is either hydrogen, air, or oxygen, perfectly dry and at a temperature of 0° C. and under a pressure of 760 mm. of mercury; these conditions of temperature and pressure are termed the standard conditions.

The specific gravity of any substance, A, is found by dividing the mass of one volume of A by the mass of one volume of the substance selected as the standard.

Let W = mass of one volume of A;
W' = mass of one volume of standard.

$$\text{Then Sp. Gr. of } A = \frac{W}{W'}.$$

Specific gravity, or, as it is frequently termed, relative mass, is entirely independent of the system of weights in which the masses of substance and standard are expressed.

Special attention should be paid to the distinction between the terms mass and weight. Mass, is the amount of matter in a substance, and is an invariable quantity; weight, expresses the force with which the substance is attracted by the earth, and varies according to the place where it is measured.

Relations between Specific Gravity, Mass, and Volume.—In the metric system the relation between the unit of mass and that of volume is an intimate one. One cubic centimetre of pure water at 4° C. has a mass of one gramme. Therefore, in all specific-gravity determinations of solids and liquids, where the values are expressed in the metric system, W' of the preceding formula may be replaced by V, signifying the volume of the water displaced.

Let W = mass of one volume of A;
V = mass of one volume of standard.

Then the formula becomes:

$$\text{Sp. Gr.} = \frac{W}{V}.$$

From this are deduced the values of W and of V:

$$W = V \times \text{Sp. Gr.};$$
$$V = \frac{W}{\text{Sp. Gr.}}.$$

In the formula,

$$W = V \times \text{Sp. Gr.}$$

Sp. Gr. stands for the specific gravity referred to water. If the Sp. Gr. is referred to hydrogen, as in the case of gases, this value must be reduced to the water standard before using it in the formula.

The Sp. Gr. of hydrogen referred to water is 0.0000896; the reduction is therefore easily effected by simply multiplying by this value. The formula then reads:

$$W = V \times \text{Sp. Gr.} \times 0.0000896.$$

The weight of one cubic decimetre or litre of hydrogen gas at the standard temperature and pressure is 0.089578 gramme, or, for all practical purposes, 0.0896 gramme.

In order to simplify calculation, Prof. von Hofmann proposed that this value be introduced into chemistry as a unit of weight. It is termed the crith. The crith is therefore defined, as the weight of one cubic decimetre (litre) of hydrogen gas at the standard temperature and pressure, and is equal to 0.0896 gramme.

Let Wc = the weight of a gas in criths;
Wg = the weight of a gas in grammes;
V = the volume of this gas in litres.
Then $Wc = V \times$ Sp. Gr.
and $Wg = Wc \times 0.0896$.

To ascertain the specific gravity of solids, liquids, and gases, numerous methods have been devised to meet the various conditions under which the determinations may be presented; but the principle underlying these devious methods, is of course always the same. The following examples will illustrate some of the more commonly occurring problems.

Determination of the Specific Gravity of Solids.

I. By the Balance.—This method is based on the principle of Archimedes: a body immersed in a liquid loses in weight, an amount equal to the weight of the liquid displaced.

a. The solid is insoluble in, and heavier than, water.

EXAMPLE:

Weight of solid in air........................ = 10.000
" " " " water........................ = 8.000

Weight of water displaced by the solid is:

$$\begin{array}{r} 10.000 \\ 8.000 \\ \hline 2.000 \end{array}$$

$$\text{Sp. Gr.} = \frac{10}{2} = 5.0.$$

b. The solid is insoluble in, and lighter than, water.

As the solid is lighter than water, there must be attached to it a piece of some other substance which is heavy enough to immerse the combination. The substance thus attached is called a sinker.

EXAMPLE:

Weight of solid in air = 25.350
“ “ sinker in air = 11.000
“ “ solid and sinker in water = 5.100
Specific gravity of sinker = 9.000

Weight of solid in air = 25.350
“ “ sinker in air = 11.000

“ “ solid + sinker in air = 36.350
Specific gravity of sinker = 9.000
Weight of sinker in air = 11.000
Volume of sinker = $\frac{11}{9}$ = 1.222

This expresses also the loss in weight the sinker would sustain if immersed alone in water.

Weight of solid + sinker in air = 36.350
“ “ “ “ “ “ water = 5.100

Loss of weight of solid + sinker in water = 31.250
“ “ “ “ sinker in water = 1.222

“ “ “ “ solid in water = 30.028

$$\text{Sp. Gr.} = \frac{25.350}{30.028} = 0.844.$$

II. By the Specific-gravity Flask (Pyknometer).—

a. The solid is insoluble in water.

This method is especially indicated in cases where the solid is in a fine state of division; for instance, in the case of a powder.

EXAMPLE:

Weight of solid in air = 10.000
“ “ pyknometer = 5.035
“ “ “ + water = 40.535
“ “ “ + solid and water* = 46.755

---

* This fills the space in the flask not occupied by the solid.

Weight of pyknometer + water................ = 40.535
“ “ “ .... = 5.035

“ “ water.............................. = 35.500

Weight of pyknometer + solid + water.......... = 46.755
“ “ “ .... = 5.035

“ “ solid + water........................ 41.720
“ “ solid .... = 10.000

“ “ water in space not occupied by the solid = 31.720

The solid therefore occupies a space of 35.50 less 31.72 = 3.78 c. c.

$$\text{Sp. Gr.} = \frac{10.00}{3.78} = 2.645.$$

b. The solid is soluble in water.

Some liquid must be used in which the solid is not soluble; alcohol, naphtha, turpentine, or oil are usually employed. The specific gravity of the liquid used, with reference to water, and the specific gravity of the solid with reference to the liquid used, must be ascertained. A multiplication of these two values represents the specific gravity of the solid with reference to water.

EXAMPLE :

Weight of solid in air.......................... = 400.00
“ “ “ “ turpentine................... = 182.50

“ “ an equal volume of turpentine....... = 217.50

Sp. Gr. of solid referred to turpentine = $\frac{400.0}{217.5}$... = 1.84
Sp. Gr. of turpentine referred to water.......... = 0.87
Sp. Gr. of solid referred to water = 1.84 × 0.87.. = 1.60

Determination of the Specific Gravity of Liquids.

I. By the Specific-gravity Flask (Pyknometer).—

EXAMPLE :

Weight of pyknometer........................... = 5.000
“ “ “ + water.................. = 20.000
“ “ “ + liquid.................. = 17.000

Weight of pyknometer + water .... = 20.000
“ “ “ .... = 5.000

“ “ water.............................. = 15.000

Weight of pyknometer + liquid................ = 17.000
“ “ “ .... = 5.000

“ “ liquid .... = 12.000

Sp. Gr. of liquid = $\frac{12.00}{15.00}$...................... = 0.80

II. By Weighing a Solid Insoluble in Water and in the Liquid, in: Air, Water, and the Liquid.—

Example:

Weight of solid in air........................ = 12.000
“ “ “ “ water........................ = 7.000
“ “ “ “ liquid...................... = 8.000

Weight of solid in air........................ = 12.000
“ “ “ “ water........................ = 7.000

“ “ water displaced.................... = 5.000

Weight of solid in air........................ = 12.000
“ “ “ “ liquid...................... = 8.000

“ “ liquid displaced.................... = 4.000

Sp. Gr. of liquid = $\frac{4.0}{5.0}$.......................... = 0.80

III. By the Method of Balanced Liquid Columns.—This method depends on the principle of the equilibrium of liquids in connected vessels. Two vertical glass tubes are connected at their upper ends with each other, and with the chamber of an air-syringe. The lower end of one of these tubes dips into water; that of the other tube dips into the liquid, the specific gravity of which is to be ascertained. The air is partially exhausted from the upper part of the two tubes, and in consequence, the water and the liquid rise. Closing the stop-cock which connects the tubes with the air-syringe, the liquids will remain standing at a certain height in their respective tubes, the two columns being in equilibrium. The specific gravity of the liquid is found, by dividing the height of the column of water by the height of the column of liquid.

EXAMPLE:

Height of column of water .... = 80 cm.
" " " " liquid .... = 60 cm.

$$\text{Sp. Gr. of liquid} = \frac{80}{60} = 1.333$$

IV. By Areometers.—This is an indirect method of ascertaining the specific gravity of fluids. The instruments employed for the purpose are made of glass or of metal. They consist of a bulb or float filled with air, a stem placed above this float and bearing a scale, and a smaller bulb, the counterpoise, placed beneath the float and weighted with mercury or shot, so as to keep the instrument in an upright position when placed in a fluid.

A body immersed in a liquid floats, when it has displaced an amount of the liquid equal in weight to its own weight. It is therefore evident, that an areometer will sink more deeply in a liquid of less density, than it will in a liquid of greater density.

Areometers are provided with scales which either indicate specific-gravity values, or else bear an arbitrary graduation.

In instruments graduated to show specific-gravity values. the spaces between successive degrees are unequal.

These areometers are constructed on the principle, that equal differences of specific gravities are indicated by quantities proportional to the differences of the reciprocals of the specific gravities.

On areometers graduated according to an arbitrary scale, the divisions are usually equal. Different kinds of areometers with arbitrary scales are employed in the arts and industries.

To determine the specific gravity of a liquid by means of an areometer, due attention being paid to the temperature of the liquid, the instrument is placed in the liquid, and that degree of the scale which is in contact with the surface of the liquid, is noted.

If the areometer is graduated according to specific-gravity values, the figure thus indicated denotes the specific gravity of the liquid. If the graduation on the instrument is according to some arbitrary scale, conversion into the corresponding specific-gravity value must be made by calculation, or else is determined by aid of tables prepared for the purpose.

AREOMETERS WITH ARBITRARY SCALES.—Among the numerous areometers provided with arbitrary scales, those devised by Antoine Baumé in 1768, and bearing his name, are probably used more extensively than any other kind.

Although Baumé described very accurately the manner in which he obtained the scales for his two instruments—the one for liquids heavier, the other for liquids lighter, than water—yet, in the course of time, the makers of these instruments deviated from his directions, and in consequence there resulted great confusion as to the actual relation between the values of the so-called Baumé degrees and specific gravity.

True Value of Baumé Degrees.—In a paper delivered by C. F. Chandler before the National Academy of Sciences in 1881, there are given no less than twenty-three different scales for liquids heavier than water and eleven different scales for liquids lighter than water, no two of which are identical, and not one of which was made in exact accordance with the original directions of Baumé. In order to ascertain the true value of these degrees in terms of specific gravity, the original French directions were secured, Baumé's experiments were most carefully repeated, and the following table, by C. F. Chandler and the author, gives, as the result of these investigations, the true values of Baumé's degrees for liquids heavier than water, calculated by the formulæ:

$$n = \frac{P \times d}{P - 1}; \qquad P = \frac{n}{n - d}.$$

In which P = the specific gravity; d = the Baumé degree; n = the modulus.* 0° = 1. and 15° = 1.1118988, by the modulus 149.04969.

[Temperature 10° R. = 12.5° C. = 54.5° F.]

Baumé Degrees.	Specific Gravity.	Baumé Degrees.	Specific Gravity.	Baumé Degrees.	Specific Gravity.
0	1.00000	26	1.21129	52	1.53580
1	1.00675	27	1.22122	53	1.55179
2	1.01360	28	1.23131	54	1.56812
3	1.02054	29	1.24156	55	1.58479
4	1.02757	30	1 25199	56	1.60182
5	1.03471	31	1.26260	57	1.61923
6	1.04194	32	1.27338	58	1.63701
7	1.04927	33	1.28436	59	1.65519
8	1.05671	34	1.29552	60	1.67378
9	1.06426	35	1.30688	61	1.69279
10	1.07191	36	1.31844	62	1.71223
11	1.07968	37	1.33021	63	1.73213
12	1.08755	38	1.34218	64	1.75250
13	1.09555	39	1.35438	65	1.77335
14	1.10366	40	1 36680	66	1.79470
15	1.11189	41	1.37945	67	1.81657
16	1.12025	42	1.39234	68	1.83899
17	1.12873	43	1.40547	69	1.86196
18	1.13735	44	1.41885	70	1.88551
19	1.14609	45	1.43248	71	1.90967
20	1.15497	46	1.44638	72	1.93446
21	1.16399	47	1.46056	73	1.95989
22	1.17316	48	1.47501	74	1.98601
23	1.18246	49	1.48975	75	2.01283
24	1.19192	50	1 50479	76	2.04038
25	1.20153	51	1.52014		

Relation between Specific Gravity, Degrees Baumé, and Degrees Brix.—An areometer which is most extensively used in the sugar industry to gauge the density of saccharine solutions, is known as the saccharometer of Balling or Brix.

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* That part of an areometer which is immersed when the instrument floats in water.

This instrument bears a scale of 100 degrees, and its readings indicate the percentage of sucrose in aqueous solutions.

Comparison between specific-gravity values, degrees Baumé, and degrees Brix, can be made by means of the following formulæ, due to von Lorenz.* The temperature at which these relations obtain, is 17.5° C.

SPECIFIC GRAVITY AND DEGREES BRIX.

Let d = specific gravity,
s = degrees Brix.

For the range of:

0°—35° Brix........................ $d = \dfrac{29374 + 14s}{29375 - 100s}$

35°—70° Brix........................ $d = \dfrac{35036 + 43s}{35163 - 100s}$

70°—100° Brix........................ $d = \dfrac{42067 + 92s}{42908 - 100s}$

DEGREES BRIX AND SPECIFIC GRAVITY.

For the range of:

1.00000—1.15411..................... $s = \dfrac{29375d - 29374}{100d + 14}$

1.15411—1.35088..................... $s = \dfrac{35163d - 35036}{100d + 43}$

1.35088—1.55785..................... $s = \dfrac{42908d - 42067}{100d + 92}$

SPECIFIC GRAVITY AND DEGREES BAUMÉ.

Let d = specific gravity,
n = degrees Baumé.

$$d = \frac{146.78}{146.78 - n}.$$

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* Oesterreichisch-Ungarische Zeitschrift für Zuckerindustrie und Landwirthschaft, 1891, Vol. XX. p. 571.

DEGREES BAUMÉ AND SPECIFIC GRAVITY.

$$n = 146.78\,\frac{d - 1}{d}.$$

DEGREES BRIX AND DEGREES BAUMÉ.

Let s = degrees Brix,
n = degrees Baumé.

For the range of:

0.00°—19.60° Baumé.................. $s = \dfrac{10 + 2097n}{1195 - n}$

19.60°—38.12° Baumé.................. $s = \dfrac{433 + 814.5n}{488 - n}$

38.12°—52.56° Baumé.................. $s = \dfrac{1342 + 457.2n}{306.3 - n}$

DEGREES BAUMÉ AND DEGREES BRIX.

For the range of:

0°—35° Brix......................... $n = \dfrac{1195s - 10}{s + 2097}$

35°—70° Brix......................... $n = \dfrac{488s - 433}{s + 814.5}$

70°—100° Brix......................... $n = \dfrac{306.3s - 1342}{s + 457.2}$

An extensive table, exhibiting the corresponding values of specific gravity, degrees Brix, and degrees Baumé for pure sugar solutions from 0 to 100 per cent, at 17.5° C., has been calculated by Mategczek and Scheibler,* and the data of this table agree very closely with the results obtained by calculation with the formulæ of von Lorenz.

Specific Gravity of Gases and Vapors.

In making determinations of the specific gravity of gases and vapors, great attention must be paid to the conditions of temperature and pressure obtaining at the time, for,

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* Loc. cit.; also, Wiechmann, Sugar Analysis.

according to the Law of Charles, *the volume of a gas varies directly as the temperature*, and, according to the Law of Mariotte,* *the volume of a gas varies inversely as the pressure.*

The standard of specific gravity of gases and vapors generally adopted is pure, dry hydrogen, or pure, dry air, at the temperature of 0° C. and under the pressure of 760 mm. of mercury.

Specific-gravity values determined in terms of one of these standards, can readily be expressed in terms of the other.

One litre of hydrogen under the standard conditions weighs 0.0896 gramme. One litre of air under the standard conditions weighs 1.293 grammes.

The specific gravity of hydrogen referred to air as standard is, therefore,

$$\frac{0.0896}{1.293} = 0.0693,$$

and the specific gravity of air referred to hydrogen as standard, is equal to,

$$\frac{1.293}{0.0896} = 14.43.$$

Hence, if the specific gravity of a gas or vapor be given in terms of hydrogen as standard, this value multiplied by 0.0693 will express its specific gravity with reference to air as standard.

If the specific gravity is referred to air as standard, the value given multiplied by 14.43 will express the specific gravity on the hydrogen basis.

The principal methods employed in the determination of the specific gravity of gases and vapors are the following.

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* Also known as the Law of Boyle.

Determination of the Specific Gravity of Gases.

I. Weighing Equal Volumes of the Standard selected and of the Gas the Specific Gravity of which is to be determined.—

a. By collecting in a vessel over mercury. (Bunsen.)

b. By displacement.

The gas the specific gravity of which is sought, is passed into a vessel of known volume, and displaces an inert gas which this vessel contains. The temperature is kept constant throughout the experiment.

c. By counterbalanced globes. (Regnault.)

These methods require the following data:

P = the weight of the empty vessel, in air.

P' = the weight of the vessel filled with the gas, in air.

V = the capacity of the vessel in cubic centimetres.

v = the volume of the residual air in cubic centimetres.

$$\left.\begin{array}{l} H = \text{height of barometer} \\ t = \text{the temperature} \end{array}\right\} \text{at which } P' \text{ is found.}$$

$$\left.\begin{array}{l} H' = \text{height of barometer} \\ T = \text{the temperature of} \\ \qquad \text{the bath} \end{array}\right\} \begin{array}{l}\text{at the time of sealing or closing} \\ \text{the vessel.}\end{array}$$

k = the coefficient of cubical expansion of the material of the vessel.

0.00367 = the coefficient of expansion of a gas at constant pressure.

The specific gravity referred to hydrogen, is calculated by the formula:

$$\text{Sp. Gr.} = \frac{P' - P + \dfrac{0.0012932\,.\,(V - v)\,.\,H}{(1 + 0.00367\,T)\,.\,760}}{\left[V(1+kT) - v\,\dfrac{1+0.00367\,.\,T}{1+0.00367\,.\,t}\right]\dfrac{H' \times 0.00008958}{760\,.\,(1+0.00367\,T)}}.$$

II. Effusion Method. (Bunsen.)—This method is based on the principle that the specific gravity of gases varies directly as the square of the time of effusion of equal volumes.*

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* Sometimes expressed in this form: The rates of effusion are inversely as the square roots of the specific gravities of the gases.

Equal volumes of the standard gas, and of the gas the specific gravity of which is to be determined, are allowed to escape through a very small aperture from the vessel in which they are contained, and the time required by each to do this, is noted.

EXAMPLE:

One volume of air effuses in 180 seconds.

One volume of gas the specific gravity of which is sought, effuses in 120 seconds.

$$180^2 : 120^2 :: 1 : x;$$
$$32400 : 14400 :: 1 : x;$$
$$x = 0.44.$$

Hence, Sp. Gr. of the gas referred to air is 0.44.

Determination of the Specific Gravity of Vapors.

The specific gravity of a vapor is usually determined by:

I. The Weighing of a Known Volume of the Vapor taken at an Ascertained Temperature and Pressure.

Methods of (*a*) Dumas,
(*b*) Deville,
(*c*) Troost.

II. The Direct Measurement of the Volume of Vapor produced by the Evaporation in a Closed Space of a Known Weight of the Substance.

Methods of (*a*) Hofmann,
(*b*) Gay-Lussac.

III. The Indirect Measurement of the Volume of Vapor produced by the Evaporation in a Closed Space of a Known Weight of the Substance, accomplished by measuring the Volume of a Liquid or of some Gas displaced by the Vapor.

Method of Victor Meyer.

I. Dumas' Method.—To calculate the specific gravity of a vapor by Dumas' method, it is necessary to ascertain the weight of a known volume of this vapor at a known temperature and under a known pressure, and to divide this value by the weight of the same volume of air, or hydrogen, at the same temperature and under the same pressure.

A glass vessel filled with dry air or hydrogen is weighed. Then the substance, the specific gravity of whose vapor is to be determined, is introduced and vaporized. When the vessel is filled completely and exclusively with this vapor, the neck of the vessel is sealed and the vessel is reweighed.

The formula by which the density of a vapor determined by Dumas' method, and referred to air as unity, is calculated, is the following:

$$\text{Specific gravity} = \frac{b + c - a}{W}.$$

In which:

a = the weight of the vessel;
b = the apparent weight of the vessel and the vapor;
c = the weight of the air displaced by the vessel;
W = the weight of an equal volume of air at the same pressure and temperature. The increased volume of the vessel at the higher temperature must of course be taken into account.

Before illustrating the application of this formula by an example, the manner of calculating some of the values used in this formula should be explained.

Suppose it were required to ascertain the weight (W) of dry air at a temperature t and at a pressure H, contained in a glass vessel whose capacity is V at 0° C.

1 c. c. dry air at a pressure of 76 cm. and at a temperature of 0° C. weighs 0.001293 gramme.

The weight of a given volume of any gas varies directly as the pressure and inversely as the temperature.

The weight of V cubic centimetres of dry air at any temperature and at any pressure other than 0° C. and 76 cm., respectively, would be calculated by the formula:

$$W = 0.001293 \cdot \frac{H}{76} \cdot \frac{273}{273 + t} \cdot V.$$

If the change in temperature is great, the capacity of the glass vessel is altered, and allowance for this must be made.

If the coefficient of expansion of the vessel is represented by k, then the preceding formula is changed to:

$$W = 0.001293 \cdot \frac{H}{76} \cdot \frac{273}{273 + t} \cdot V(1 + tk).$$

Should the weight of dry hydrogen be required instead of dry air, as here calculated, the value 0.0000896, the weight of 1 c. c. dry hydrogen at 0° C. and at 76 cm., must be substituted for the value 0.001293 in above formula.

If the calculation is to be made by logarithms, the formula can be cast into the following form :

For air :

$$\log. W = 7.6670 + \log. H + \text{ar. co. log.}\,(273 + t) + \log. V + \log. (1 + tk) - 20.$$

For hydrogen :

$$\log. W = 6.5077 + \log. H + \text{ar. co. log.}\,(273 + t) + \log. V + \log. (1 + tk) - 20.$$

The constant in above formula, for air, viz., 7.6670, is thus obtained:

The formula previously given contains the constant quantities $0.001293 \cdot \frac{273}{76}$.

To abbreviate the calculation, the value for this expression has been figured as follows:

$$\begin{array}{lr}
\log. 0.001293 = & .111599 - 3 \\
\log. 273 \qquad = & 2.436163 \\
\text{ar. co. log. } 76 = & 8.119186 - 10 \\
\hline
 & .666948 - 3 \\
\hline
 & \bar{3}.666948 \\
 & +\,10.000000 \\
\hline
 & 7.666948\ (-\,10.)
\end{array}$$

which can be contracted to 7.6670 (− 10.)

The value for hydrogen, 6.5077, is obtained in the same manner.

The following will illustrate the calculation of a vapor density determination by Dumas' method:

EXAMPLE: Calculate from the following data the specific gravity of camphor vapor referred to air as standard:

Weight of glass vessel .... $a = 50.134$ grs.
Height of barometer .... $H = 74.2$ cm.
Temperature .... $t = 13.5°$ C.
Weight of vessel and vapor .... $b = 50.842$ grs.
Height of barometer .... $H' = 74.2$ cm.
Temperature .... $t' = 244°$ C.
Volume .... $V = 295$ c. c.
Coefficient of expansion of glass .... $k = 0.000025$.

As previously stated, specific gravity $= \dfrac{b + c - a}{W}$.

Calculation of c:

Constant log.	7.6670 − 10.
$H = 74.2$ log.	1.8704
$273 + t = 286.5$ ar. co. log.	7.5428 − 10.
$V = 295$ log.	2.4698
	$\bar{1}.5500$

$c = 0.3548$

Calculation of W:

Constant log.	7.6670 − 10.
$H' = 74.2$ log.	1.8704
$273 + t' = 517$ ar. co. log.	7.2865 − 10.
$V = 295$ log.	2.4698
$(1 + 244 \times 0.000025) = 1.0061$ log.	0.0025
	$\bar{1}.2962$
$b =$	50.842
$c =$	0.3548
$b + c =$	51.1968
$a =$	50.1340
$(b + c - a) =$	1.0628
W log. = ...	9.2962
$(b + c - a)$ log. = ...	10.0265
	0.7303

Number log. 0.7303 = 5.374

Hence, specific gravity sought = 5.374

II. Hofmann's Method.—This method is particularly applicable in dealing with substances of comparatively low boiling point. It bases on the observation of the volume and the tension of vapor produced from a weighed amount of substance.

The apparatus consists of a graduated glass tube, which is first filled with mercury and then inverted over a mercury trough. The mercury on falling to its proper level, leaves a vacuous space in the upper part of the tube. This tube is jacketed by another tube of glass, so made that steam, or the vapor of some liquid boiling at a higher temperature than water, can be kept playing about the enclosed tube.

A small quantity of the substance the vapor density of which is to be determined, is weighed off, passed up through the mercury and is thus introduced into the space above. There it vaporizes, and, in consequence of its tension, depresses the mercury column.

This depression of the mercury as well as the barometric pressure and the temperature obtaining at the time are noted, and these values, together with the weight of the substance taken, furnish all the data necessary for the calculation.

Referred to hydrogen as standard, the specific gravity of the vapor can be calculated by the formula:

$$\text{Sp. Gr.} = \frac{w \,.\, 760 \,.\, (1 + 0.00367\,T)}{v \,.\, 0.00008958 \,.\, (H - h) \,.\, (1 + kT)},$$

where w = weight of substance taken, and hence weight of vapor formed;

v = observed volume of vapor expressed in cubic centimetres;

H = reduced height of barometer at time of experiment;

h = reduced height of mercury in tube above that in trough;
T = temperature of vapor;
k = coefficient of cubical expansion of glass.

Or, calculation can be effected by the formula: Sp. Gr. $= \frac{w}{W}$ where W represents the weight of an equal volume of air, under conditions identical with those under which the volume of the vapor was determined.

EXAMPLE: Calculate from the following data the specific gravity of chloroform vapor referred to air as standard:

Weight of substance, and hence Weight of vapor	$w = 0.2500$ gr.
Volume of vapor	$V = 110$ cc.
Height of barometer	$H = 75.62$ cm.
Reduced height of mercury in tube above that in trough	$h = 32.25$ cm.
Temperature of vapor	$T = 100°$ C.

Solving by means of logarithms, the value of W is found by the formula:

$$\log. W = 7.6670 + \log. (H - h) + \text{ar. co. log.} (273 + t) + \log. V + \log. (1 + t\,0.000025) - 20.$$

Constant log.	7.6670 − 10.
$H - h = 43.37$ log.	1.6372
$273 + t = 373$ ar. co. log.	7.4283 − 10.
$V = 110$ log.	2.0414
$(1 + 100 \times .000025)$ log.	0.0008
	8.7747 − 10.
$w = 0.2500$ log.	9.3979 − 10.
	0.6232

Number log. 0.6232 = 4.20
Hence, specific gravity of vapor sought = 4.20.

III. Victor Meyer's Method.—This method, which is equally well adapted for vapor-density determinations of substances with a high, as for those with a low, boiling-point, is the method now generally employed.

A weighed amount of substance is vaporized in a vessel which contains air.

The vapor displaces an equal volume of air, and this expelled volume of air is measured.

The apparatus consists of a jacketed glass cylinder of about 100 cubic centimetres capacity which opens into a narrow glass tube that is provided with a well-fitting glass stopper. A little below this stopper, a short branch-tube is attached, which leads into a water-trough and which terminates under a graduated glass vessel, an eudiometer, filled with water.

To make a determination with this apparatus, the jacket surrounding the glass cylinder is filled with a liquid of known boiling-point. The liquid selected for this purpose of course has a boiling-point higher than that of the substance the vapor density of which is to be ascertained.

A small amount of the substance to be examined is weighed out, placed into a small stoppered tube or bulb, and is introduced into the jacketed cylinder, where it is vaporized. The vapor produced expels an equal volume of air; this, in turn, displaces some of the water in the eudiometer, being itself thus confined and measured.

The calculation is simple. The specific gravity of the vapor is equal to the weight of the vapor (the weight of the substance used), divided by the weight of an equal volume of air, i.e., by the weight of the air expelled.

Expressed in a formula, taking air as standard, it would be:

$$\text{Sp. Gr.} = \frac{w\,.\,(1 + 0.00367\,T)\,.\,760}{0.001293\,.\,v\,.\,(H - p)};$$

and, taking hydrogen as standard,

$$\text{Sp. Gr.} = \frac{w \,.\, (1 + 0.00367\,T) \,.\, 760}{0.00008958 \,.\, v \,.\, (H - p)},$$

in which formulæ,

w = weight of substance taken;
v = the observed volume of displaced gas in cubic centimetres;
H = reduced height of barometer at time of experiment;
p = tension of aqueous vapor at the temperature of the measuring vessel.
T = temperature of the water in the collecting trough.

Calculation of determinations made by Victor Meyer's method, can of course also be effected by logarithms.

The value sought, specific gravity referred to air as standard, can be calculated by the formula:

$$\text{log. Sp. Gr.} = \text{log. } w - \text{log. } w',$$

where w = weight of vapor,
w' = weight of displaced air,

and where the value of log. w' is found by the expression,

$$\text{log. } w' = 7.6670 - \text{log. } (H - p) + \text{ar. co. log. } (273 + t) + \text{log. } V - 20.$$

Or, the specific gravity can also be calculated by use of the following expression:

$$\text{log. Sp. Gr.} = 2.3330 + \text{ar. co. log. } (H - p)$$
$$+ \text{log. } (273 + t) + \text{ar. co. log. } V + \text{log. } W - 20.$$

The value 2.3330 is obtained by subtracting the constant 7.6670 from 10.0000.

EXAMPLE Calculate from the following data the specific gravity of carbon disulphide referred to air as standard:

$w =$ .... 0.0495 gr.
$v =$ .... 16.4 c. c.
$H =$ .... 71.78 c. m.
$p =$ .... 1.40.
$T =$ .... 16.5° C.

Log. Sp. Gr. $= 2.3330 +$ ar. co. log. $(H-p) +$ log. $(273+t)$ $+$ ar. co. log. $v +$ log. $w - 20$.

2.3330
$(H-p)$ ar. co. log .... $8.1525 - 10$
$(273+t)$ log 2.4617
ar. co. log. v .... $8.7852 - 10$
log. w .... $\bar{2}.6946$
0.4270

Number log. 0.4270 = 2.673.
Hence, specific gravity of vapor = 2.673.

CHAPTER III.

CHEMICAL NOMENCLATURE AND NOTATION.

THE development of the language of chemistry, conditioned as it has been by the evolution of the science, presents an interesting subject for study.

Earliest Times.—The oldest chemical terms were either very general, or else suggestive of the origin of the substances to which they were applied.

Since the earliest times, the term "sal" has been used for everything having a salty taste; since the eighth century the kind or origin of the substance was indicated by an additional word; for instance, "sal maris."

In Geber's writings there is no attempt at any system in the naming of chemical bodies; whether or not he was familiar with the use of any of the symbols for the metals which were used by the alchemists in later times, is very doubtful. They are certainly to be found in his works, but as these consist almost exclusively of Latin translations made in the sixteenth century, it is an open question whether they appeared in the original, or were inserted by the translators.

Notation of the Alchemists.—With the thirteenth century the alchemists commenced to use certain symbols quite freely.

The seven metals, gold, silver, mercury, copper, iron, tin, lead, were known by the following names and symbols:

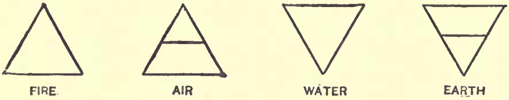
Gold = Sol ☉
Silver = Luna ☽
Mercury = Mercurius ☿
Copper = Venus ♀

Iron = Mars ♂
Tin = Jupiter ♃
Lead = Saturnus ♄

Concerning the meaning of these symbols but little is known; the exact time when they were brought into use can also not be determined.

It has been suggested that the symbol for Saturnus represented his scythe, the symbol for Mars his shield and spear, the symbol for Venus her hand-mirror. Some of the alchemists believed that these symbols were indicative of the chemical peculiarities of the metals they represented. Thus the circle was regarded as illustrating perfection of the metallic state, the semicircle an approximation to this condition, and so on.

Since the thirteenth century the following signs were employed to designate the four elements of Aristotle:



Gradually other symbols found their way into alchemistical writings, but few of these met with general acceptance. Since the fourteenth century sulphur is quite generally found represented by the symbol 🜍.

Attempts made in the period beginning with the thirteenth and extending to about the eighteenth century, to generalize terms of chemical substances, led to much trouble and confusion.

The principal physical properties of substances were important considerations in their naming. For instance, to everything fluid the term "mercurius" was given; pure mercury was "mercurius communis;" alcohol was known as "mercurius vegetabilis." Viscous liquids received the appellation "oleum;" thus, for instance, "oleum tartari" and "oleum vitrioli," to which latter term oil of vitriol is directly traceable.

According to their different tastes, salts were distinguished as "salia acida" and "salia alcalina;" according to their volatility or non-volatility, they were divided into "salia alcalina fixa" and "salia alcalina volatilia."

A yellow or yellowish-red metallic compound was called "crocus;" a black compound was termed "æthiops."

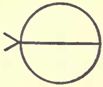
Nomenclature in the Seventeenth Century.—In the seventeenth century, when the number of compounds known increased rapidly, the names of the discoverers of these substances were frequently used as an aid in distinguishing between them. The practice of having similar names indicate similarity of properties, originated only towards the end of this epoch.

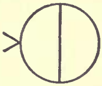
All sulphuric-acid salts were then designated as "vitriols;" nitric-acid salts came to be known as "salpetres." As a rule, similarity in terminology referred to the acid of the compound; salts consisting of the same base with different acids, were rarely indicated by similar-sounding names.

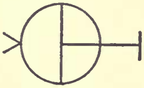
In the beginning of the eighteenth century several attempts were made to introduce chemical signs and symbols which should express concisely the nature of substances.

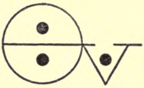
Geoffrey in 1718 used the customary symbols for the metals, and in addition introduced the following signs:

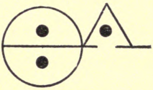
Acids .... = 

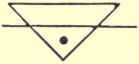
HCl .... = 

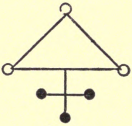
HNO_3 .... = 

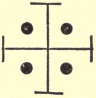
H_2SO_4........... = 

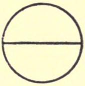
Fixed Alkali..... = 

Volatile Alkali... = 

Absorbing Earths = 

Phlogiston
Principe huileux } = 
Soufre principe

Vinegar.......... = 

Salt............. = 

Alcohol.......... = 

Bergman's System.—About the middle of the eighteenth century Macquer and Baumé strongly emphasized the necessity of designating substances similar in composition, by similar names. Their efforts were supported in 1770 by Bergman, who advocated a new system of nomenclature, based however, as far as possible, on the terms then in vogue. He made various suggestions as to how this could be accomplished, but was himself not very consistent in the adoption and use of these terms.

In 1780 Bergman also proposed to use similar symbols for bodies analogous in composition. each body to be designated by some specific symbol.

The four elements and the two combustible bodies, sulphur and phosphorus, were to be indicated by triangles drawn in different ways. Metallic bodies (*regulos*) were to be represented by a crown; a circle was to denote salts and alkalies, a cross the acids.

To Bergman is also due the first attempt to use compound symbols which were intended to indicate the nature of chemical combinations.

The compound salts were to be expressed by the name of the alkali which they contained, together with an adjective formed from the name of the acid. The following will explain:

Modern Symbols.	Bergman's Appellation.
K_2SO_4	Alkali vegetabile vitriolatum.
Na_2SO_4	Alkali fossile vitriolatum.
$(NH_4)_2SO_4$	Alkali volatile vitriolatum.
KNO_3	Alkali vegetabile nitratum.
$NaNO_3$	Alkali fossile nitratum.
NaCl	Alkali fossile salitum.
Etc.,	etc.

Black's List of Synonyms.—That endless confusion reigned in the matter of chemical nomenclature by this time, and how pressing was the need of reform, is most strikingly shown by the list of the "most usual synonimes" given in Dr. Joseph Black's "Lectures on the Elements of Chemistry, etc.," Vol. II. p. 148 (first American from the last London edition, 1806, Philadelphia).

The following are the synonyms there given for potassium, sodium, and ammonium. The other substances enumerated in Black's list, rejoice in from two to eleven synonyms each.

Salium Alkalinorum Synonima.

Potassium.

1. Lixiva.
2. Alkali fixum vegetabile.
3. Kali. Pharm. Lond.
4. Potassa. Gallis.
5. Sal tartari.
6. Sal absynthii.
7. Cineres clarellati. Nitrum fixatum.
8. Oleum tartari.
9. Lixivium tartari.
10. Aqua kali. Lond.

Sodium.

1. Trona.
2. Alkali fixum fossile.
3. Soda. Pharm. Edin.
4. Natron. Lond.
5. Soda. Gallis.

Ammonium.

1. Ammonia.
2. Alkali volatile. Edin.
3. Ammonia. Lond.
4. Ammoniaca. Gallis.
5. Sal volatile ammoniaci.
6. Sal cornu cervi.
7. Sal urinæ.
   Aqua dilutum.
8. Spiritus salis ammoniaci.
9. Aqua ammoniæ.
10. Spiritus cornu cervi.
11. Spiritus urinæ.

French Systems of Nomenclature.—The system of Bergman met with quite universal favor; but when the phlogiston theory was overthrown and Lavoisier's dualistic theory carried the field, a new system of nomenclature became imperative.

The method proposed by Bergman, to have the nomenclature reduced to some system valid for the whole of chemical science, and which system should be applicable to each and every new addition to the science, was retained, while the construction of the nomenclature was changed so as to meet the wants of the newly-formed "French Chemistry."

In 1782 Guyton de Morveau published in the *Journal de*

Physique an outline of a system of chemical nomenclature. This was based on the phlogiston theory, but bore in it some of the features which are retained in the system used at the present time.

De Morveau distinguished clearly between acids, bases, and salts. The acids all received the term "acides" and were distinguished from one another by adjectives which indicated the kind of acid; for instance, acide vitriolique, acide nitreux, acide oxalique, etc.

The salts were named from the acid and the base that formed them; for instance, vitriol de cuivre, fleur de calce, nitre de mercure. Among the bases he counted the metals, alcohol, and phlogiston.

In 1787 Lavoisier, Morveau, Berthollet, and Fourcroy presented to the French Academy a detailed plan of a new system of nomenclature. This memoir was entitled "Méthode de Nomenclature Chimique. Proposée par MM. de Morveau, Lavoisier, Berthollet, et De Fourcroy," and was published in Paris in 1787, "Sous le Privilége de l'Académie des Sciences."

The elements, or, as the authors call them, simple substances, "those which up to the present time have not been decomposed," are divided into five classes.

Class I. "embraces those bodies [*principes*] which, without exhibiting among themselves a well-marked analogy, have nevertheless this in common, that they seem preferably to approach the elementary condition [*l'état de simplicité*] which causes them to resist analysis and at the same time renders them so active in combinations."

This class consists of five bodies: light (*la lumière*), heat-matter (*la matière de la chaleur*), dephlogisticated or vital air (*l'air appelé d'abord déphlogistiqué, puis air vital*), inflammable gas (*le gaz inflammable*), and phlogisticated air (*l'air phlogistiqué*).

To these substances the memoir assigns the following names:

lumière = lumière.
matière de la chaleur = calorique.
l'air déphlogistiqué, air vital = oxigène.
gaz inflammable = hidrogène.
l'air phlogistiqué = azote, from the Greek α (no) and ζωή (life).

Class II. "All acidifiable bases or radical principles of the acids."

Among these were classed nitrogen, carbon, sulphur, phosphorus, the "muriatic" radical, the "boracic" radical, etc. This class embraces twenty-six bodies, again including nitrogen.

Class III. consists of those bodies "the principal characteristic of which is to exhibit the metallic condition." This class contains seventeen bodies. Among these are named: arsenic, molybdenum, tungsten, manganese, nickel, cobalt, bismuth, antimony, platinum, and gold.

Class IV. is assigned to the five earths, which are enumerated as follows: la silice, l'alumine, la baryte, la chaux, la magnésie. Class V. consists of the three alkalies, potassium, sodium, ammonium.

In addition to these five classes, an appendix is provided which contains "those more compound substances which combine in the manner in which the elements combine, or without undergoing sensible decomposition."

This appendix contains seventeen divisions, and among the substances enumerated are mucilage, gluten, sugar, starch, resin, alcohol, ethers, and soaps.

It was the aim of those who proposed this system of nomenclature that the names given to compounds should:

indicate the body,
define it,

recall its constituent parts,
classify it according to its composition,
indicate, in a manner, the relative proportion of its constituents.

Thus, for instance, to quote an example given in this memoir:

Sulphuric acid is to designate sulphur saturated to its utmost with oxygen.

Sulphurous acid is to represent sulphur joined to a less amount of oxygen.

Sulphate is to be the name of all salts formed from sulphuric acid.

Sulphite is to be the name of all salts formed from sulphurous acid.

Sulphide is to indicate all combinations of sulphur not brought to the acid state (i.e., not combined with oxygen).

This will suffice to give an idea of how much the chemical nomenclature of to-day owes to the labors of Lavoisier, De Morveau, and their associates.

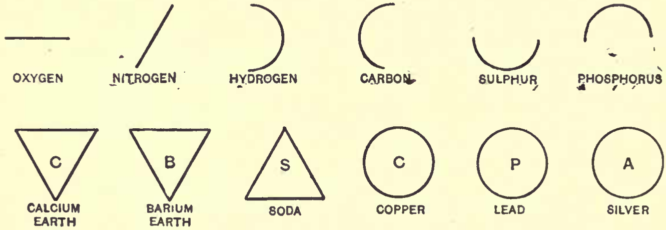
This publication contains also a most valuable " Synonimie ancienne et nouvelle par ordre alphabétique," and a " Dictionnaire pour la nouvelle Nomenclature Chimique."

Symbols of Hassenfratz and Adet.—Appended to this work and indorsed by its authors, is given a system of chemical symbols by Hassenfratz and Adet, of course adapted to the anti-phlogistic theory.

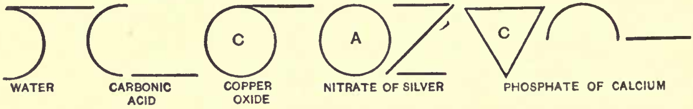
The elementary bodies are represented by simple symbols; the metals, for instance, by circles into which the first letter of their Latin name is placed, to distinguish them one from the other. All alkalies and earths are indicated by triangles placed in different positions.

Oxygen, nitrogen, hydrogen, etc., are denoted by lines, straight or curved.

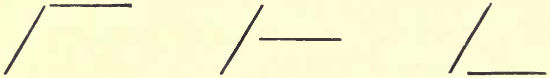
The following are a few of the symbols employed:



Compounds are indicated by combinations of symbols like the above. For instance:



The authors of this system also attempted to depict by their symbols differences in the constitution of compounds formed from the same constituents. This they sought to accomplish by the position which the several symbols were made to occupy relatively to each other. For instance, the following was intended to indicate the different steps of oxidation of nitrogen to nitric acid:



Other Systems Proposed.—The system of nomenclature of Lavoisier, De Morveau, and their colleagues, was appreciated and adopted by many chemists in France and in other countries; but opponents to it were also not lacking.

The adherents of the phlogiston theory naturally opposed it; but even others, among them Sir Humphry Davy, did not favor its acceptance. The latter made some suggestions concerning the subject, which suggestions however, did not find general approval.

It is not feasible to enumerate in detail the various propositions that were made in this connection, from all sides. As Dr. Black stated in his "Lectures on Chemistry," previously cited: "When this rage for reformation and unioration was going round it was natural for every person to think a little on the subject, and consider what he would propose were it required of him to give his opinion."

Thomson in 1804 suggested that the different stages of oxidation be denoted by prefixes; e.g., protoxyd, deutoxyd, peroxyd, etc.

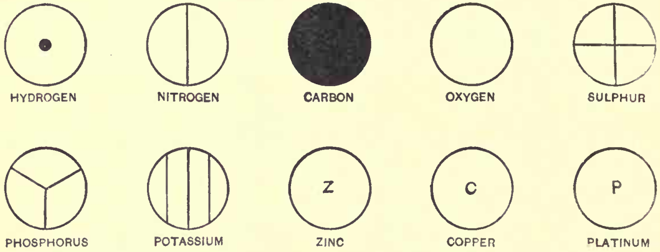
One attempt was made, some years later, to create a chemical nomenclature to be used by all nations of Germanic descent.

Oxygen was to be known as "Eld" (from the Danish *Ild*, i.e., fire). "Eldluft" represented oxygen-gas; "Elden" meant to oxidize. Hydrogen was termed "Brint" (derived from *brennen*, to burn); alkali was denoted by the word "Aesch;" etc.

In 1808 Dalton published his "New System of Chemical Philosophy." In this he represents the atoms of the different elements by circles, and these circles are provided with some distinguishing mark.

He conceived the atoms as being spheriform, and in this respect his system differs from that of Hassenfratz and Adet, who had reserved the circle as a symbol for the metals, without, however, intending to convey thereby any notion as to the configuration of the atoms. All of Dalton's circles did not bear the initial of the name of the element to be represented;

instead, he used in many instances dots and lines, as the following symbols show:

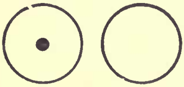


He, moreover, assigned to each symbol the duty of representing the weight of the element, according to a table of atomic weights which he published in this work.

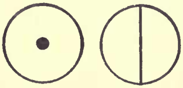
He chose hydrogen as unit, nitrogen = 5, carbon = 5, oxygen = 7, sulphur = 13, and so on.

His symbols of compounds therefore not only indicated the elements of which the compounds consisted, but illustrated as well, according to his views, their quantitative composition. The following represent respectively:

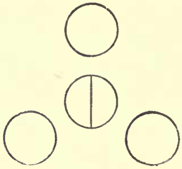
WATER.



AMMONIA.



NITRIC ACID.



In 1811 Berzelius published in the *Journal de Physique* an article which explained his views concerning chemical nomenclature. His scheme rested to a great extent on the system published by Lavoisier and his colleagues, and was originally expressed in the Latin language. It is the system essentially yet in vogue at the present day.

His system of notation permitted of the writing of chemical formulæ, which came into use in 1815. The abbreviated mineralogical formulæ had already been introduced by him in 1814.

The use of the symbols of Berzelius is retained to the present day; the initial, or the initial and the following, or, the initial and the last letter, of the name of an element, denote the element.

In his mineralogical formulæ Berzelius indicated the number of atoms of oxygen by a corresponding number of dots placed over the letters; a bar drawn through the letter or letters indicated two atoms of the element designated. Thus:

$\dot{\not{\mathrm{C}}}\mathrm{u} = \mathrm{Cu_2O}$, Cuprous oxide.

$\ddot{\mathrm{P}}\mathrm{b} = \mathrm{PbO_2}$, Plumbic oxide.

$\overset{\cdot}{\mathrm{Ca}}\ddot{\mathrm{C}} = \mathrm{CaO,CO_2}$, Calcic carbonate.

System of the Present.—At the present time there is still considerable diversity of opinion concerning chemical nomenclature. Within the past decade, and especially quite recently, several important attempts have been made to bring about a thorough reform in these matters, and these efforts, it is to be hoped, will ultimately lead to the universal acceptance by all nations of some one system of chemical nomenclature and notation.*

The principles of nomenclature which follow below, in broad outline, are those now quite generally accepted.

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* See Proceedings of International Commission for the Reform of Chemical Nomenclature, Geneva, 1892.

Le Moniteur Scientifique, Dr. Quesneville, 1892, p. 401. The Chemical News, vol. 65, p. 277.

NAMES AND SYMBOLS OF THE ELEMENTS.—The few elements which were known to the ancients, retain their appellation of old; the names of the elements more recently found, have been given by their discoverers without conformity to any rule or regulation, excepting, that if the element is a metal its name receives the termination *um*, if a non-metal, the termination *ine*, *on*, or *gen*.

Some elements have received the name of a country, like Columbium, Gallium, Germanium. In other instances they have been named from some deity; thus, Thorium is derived from Thor, the Norse god; Tantalum recalls a figure of Greek mythology.

Frequently some characteristic property of the element has suggested the name which it received. Thus, Iodine is derived from the Greek *ἴον*, a violet; Iridium, from the Latin *iris*, rainbow; Barium from the Greek *βαρύς*, heavy.

At times the planets have been selected as sponsors, as in the case of Mercury; Tellurium is named from the Latin *tellus*, the earth, and Selenium from the Greek *σελήνη*, the moon.

The symbols of the elements are abbreviated designations of their names. These symbols consist of the first, or of the first and some one additional letter of the Latin, or other, name of the element; thus, C, represents carbon; Co, cobalt; and Cu, copper,—this last symbol being derived from the Latin word *cuprum*.

The symbol of an element stands not only for the name of that element, but represents a definite amount of the same—one atom. If more than one atom is to be indicated, the required numeral is placed with the symbol, either before it, or else immediately after and a little below the symbol. This same plan is followed in expressing the composition of compounds.

NAMES OF COMPOUNDS.—The names of compounds are intended to express, as far as possible, the constitution of the substance.

If the compound consists of only one metal and one non-metal, the non-metal, receiving the termination *ide* furnishes the group name, and the metal the specific name. Thus, all compounds of metals with chlorine alone, are termed chlorides; all compounds of metals with sulphur alone, sulphides; but sodium chloride and silver sulphide denote, respectively, but one particular compound.

If two elements combine with each other in two different proportions, the termination *ic* is given to the name of the metal in that combination which contains most of the non-metal, and the termination *ous* is given to the name of the metal in that combination which contains least of the non-metal.

Thus, Cu_2O is cuprous oxide, and CuO is cupric oxide. In the latter, one atom of oxygen is combined with one atom of copper; in the former, there is but one half as much oxygen for each atom of copper present. If the ratio of two elements is as $1 : 1\frac{1}{2}$, the term *sesqui* is used to denote this relation. Thus:

$FeCl_2$ = ferrous chloride;
Fe_2Cl_6 = sesquichloride of iron; usually termed, ferric chloride.

If a given amount of one element forms several combinations with some other element, Latin or Greek numerical prefixes are employed to distinguish the compounds. Thus:

N_2O = nitrogen monoxide;
N_2O_2 = " dioxide;
N_2O_3 = " trioxide;
N_2O_4 = " tetroxide;
N_2O_5 = " pentoxide.

The terminations *ic* and *ous* are also used to distinguish acids consisting of the same elements, but containing these elements in different proportions. If combinations of the same elements exist in more than two proportions, use is made of Latin or Greek prefixes in addition to employing the endings *ic* and *ous*. Thus:

$HClO$ = [*] hypochlorous acid;
$HClO_2$ = chlorous acid;
$HClO_3$ = chloric acid;
$HClO_4$ = [†] perchloric acid.

Salts formed from *ic* acids receive the termination *ate*.

Salts formed from *ous* acids receive the termination *ite*.

Salts of *hypo-* and *per-* acids retain these prefixes, but otherwise obey the rule just stated.

Thus, the sodium salts of the acids above enumerated, are:

$NaClO$ = sodium hypochlorite;
$NaClO_2$ = " chlorite;
$NaClO_3$ = " chlorate;
$NaClO_4$ = " perchlorate.

Among other prefixes occasionally employed there should be noted: *meta*, signifying "near to;" *para*, signifying "equal;" *sub*, signifying that the compound, to the name of which this word is prefixed, contains less of a constituent than the name otherwise implies. Thus, cuprous oxide, Cu_2O, was formerly termed suboxide of copper, to distinguish it from CuO, which was known as the oxide of copper.

The intention of having the name of a substance indicate its composition has received its widest application in the chemistry of the carbon compounds.

Thus, von Hoffmann proposed the following scheme for the naming of the hydrocarbon series:

All members of the C_nH_{2n+2} series receive names terminat-

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[*] From ὑπό, under.

[†] From ὑπέρ, over.

ing in *ane* ; all of the series C_nH_{2n} have names ending in *ene*; those of the C_nH_{2n-2} series bear the ending *ine*, of the C_nH_{2n-4} series, the ending *one*, and of the C_nH_{2n-6} series, the ending *une*.

Furthermore, with the exception of the first four members of the series, which are allowed to retain their original, arbitrary, appellations, the Latin numeral which indicates the number of carbon atoms in the compound, determines the name of the compound, as the following list shows:

C_nH_{2n+2}	C_uH_{2n}	C_nH_{2n-2}
Methane...CH_4	Methene.. CH_2	
Ethane....C_2H_6	Ethene ...C_2H_4	Ethine ....C_2H_2
Propane...C_3H_8	Propene....C_3H_6	Propine....C_3H_4
Butane ...C_4H_{10}	Butene....C_4H_8	Butine.....C_4H_6
Pentane ...C_5H_{12}	Pentene ...C_5H_{10}	Pentine....C_5H_8
Hexane....C_6H_{14}	Hexene.....C_6H_{12}	Hexine....C_6H_{10}
Heptane...C_7H_{16}	Heptene...C_7H_{14}	Heptine ...C_7H_{12}
Octane ....C_8H_{18}	Octene.....C_8H_{16}	Octine.....C_8H_{14}

C_nH_{2n-4}	C_nH_{2n-6}
Propone...C_3H_2	
Butone....C_4H_4	Butune....C_4H_2
Pentone...C_5H_6	Pentune...C_5H_4
Hexone....C_6H_8	Hexune ...C_6H_6
Heptone...C_7H_{10}	Heptune...C_7H_8
Octone.... C_8H_{12}	Octune....C_8H_{10}

American Spelling and Pronunciation of Chemical Terms.—In view of the great importance attaching to the matter, it seems desirable to reproduce here a complete summary of the rules for the spelling and the pronunciation of chemical terms that were adopted by the American Association for the Advancement of Science in 1891.

This summary has been arranged in the form of a chart that is issued by the Bureau of Education, Department of the Interior, Washington, D. C., for general distribution to high schools and colleges, and following is an authorized transcript of its contents:

In 1887 a committee was appointed by the American Association for the Advancement of Science to consider the question of attaining uniformity in the spelling and pronunciation of chemical terms. The work of this committee extended through the following four years. As a result of widespread correspondence and detailed discussion at the annual meetings of the Chemical Section of the American Association, the accompanying rules have been formulated and adopted by the Association. They are submitted to chemists generally, and especially to the large number of those engaged in teaching chemistry, with the request that a cordial and earnest effort be made to render their use general and thus obviate the many difficulties arising from the present diversities of style.

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EDWARD HART, Ph.D.,
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University Club, New York City.

JAS. LEWIS HOWE, Ph.D., M.D.,
Polytechnic Society, Louisville, Ky.

Committee.

General Principles of Pronunciation.—1. The pronunciation is as much in accord with the analogy of the English language as possible.

2. Derivatives retain as far as possible the accent and pronunciation of the root word.

3. Distinctly chemical compound words retain the accent and pronunciation of each portion.

4. Similarly sounding endings for dissimilar compounds are avoided (hence **-id, -ite**).

Accent.—In polysyllabic chemical words the accent is generally on the antepenult; in words where the vowel of the penult is followed by two consonants, and in all words ending in **-ic**, the accent is on the penult.

Prefixes.—All prefixes in strictly chemical words are regarded as parts of compound words, and retain their own pronunciation unchanged (as, ă'ceto-, ă'mĭdo-, ă'zo-, hȳ'dro-, ī'so-, nī'tro-, nītrō'so-).

Elements.—In words ending in **-ium**, the vowel of the antepenult is short if i (as, īrĭ'dium), or **y** (as, dĭdy̆'mium), or if before two consonants (as, că'lcium), but long otherwise (as, tĭtā'nium, sĕlē'nium, chrō'mium).

alū'minum
a'ntimony
a'rsĕnic
bā'rium
bi'smuth (biz)
bō'ron
brō'mĭn
că'dmium
că'lcium
ca'rbon
cē'rium
cē'sium
chlō'rin
chrō'mium
cō'balt
colū'mbium

co'pper
dĭdy̆'mium
e'rbium
flū'orĭn
gă'llium
germā'nium
glū'cinum
gold
hȳ'drogen
ĭ'ndium
ī'odĭn
īrĭ'dium
iron
lă'nthanum
lead
lĭ'thium

magnē'sium (zhium)
ma'nganese (eze)
me'rcury
mōly̆'bdenum
nĭ'ckel
nī'trogen
ŏ'smium
ŏ'xygen
pallā'dium
phŏs'phorus
plă'tinum
potă'ssium
rhō'dium
rubĭ'dium
ruthē'nium
samā'rium

scă′ndium
sĕlē′nium
sĭ′licon
silver
sō′dium
strŏ′ntium (shium)
sŭ′lfur
tă′ntalum
tellū′rium
te′rbium
thă′llium
thō′rium
tin
tĭtā′nium
tŭ′ngsten
ūrā′nium
vănā′dium
ytte′rbium
y′ttrium
zinc
zircō′nium

Also: ămmō′nium, phosphō′nium, hă′logen, cȳă′nogen, ămĭ′dogen.

Note in the above list the spelling of the halogens, cesium and sulfur; **f** is used in the place of **ph** in all derivatives of sulfur (as, sulfuric, sulfite, sulfo-, etc.).

Terminations in -ic.—The vowel of the penult in polysyllables is short (as, cȳă′nic, fūmă′ric, arsĕ′nic, silĭ′cic, īŏ′dic, būtȳ′ric), except (1) **u** when not used before two consonants (as, mercū′ric, prŭ′ssic), and (2) when the penult ends in a vowel (as, benzō′ic, olē′ic); in dissyllables it is long except before two consonants (as, bō′ric, cĭ′tric). Exception: acē′tic or acĕ′tic.

The termination **-ic** is used for metals only where necessary to contrast with **-ous** (thus avoid aluminic, ammonic, etc.).

Terminations in -ous.—The accent follows the general rule (as, plă′tinous, sŭ′lfurous, phŏ′sphorous, coba′ltous). Exception: acē′tous.

Terminations in -ate and -ite.—The accent follows the general rule (as, ă′cetāte, vă′nadāte). In the following words the accent is thrown back: ă′bietāte, ă′lcoholāte, ă′cetonāte, ă′ntimonīte.

Terminations in -id (formerly -ide).—The final **e** is dropped in every case and the syllable pronounced **ĭd** (as, chlō′rĭd, ī′odĭd, hȳ′drĭd, ŏ′xĭd, hȳdrŏ′xĭd, sŭ′lfĭd, ă′mĭd, ă′nilĭd, mūrĕ′xĭd).

Terminations in -ane, -ene, -ine, and -one.—The vowel of these syllables is invariably long (as, mĕ'thāne, ĕ'thāne, na'phthalēne, a'nthracēne, prō'pīne, quĭ'nōne, ă'cetōne, kē'tōne).

A few dissyllables have no distinct accent (as, benzēne, xȳlēne, cētēne).

The termination **-ine** is used only in the case of doubly unsaturated hydrocarbons, according to Hofmann's grouping (as, propīne).

Terminations in -in.—In names of chemical elements and compounds of this class, which includes all those formerly ending in **-ine** (except doubly unsaturated hydrocarbons), the final **e** is dropped, and the syllable pronounced **-in** (as, chlō'rĭn, brō'mĭn, etc., ă'mĭn, ă'nilĭn, mo'rphĭn, quĭ'nĭn (kwĭ'nĭn), vanĭ'llĭn, alloxă'ntĭn, absi'nthĭn, emŭ'lsĭn, căffeĭn, cō'caĭn).

Terminations in -ol.—This termination, in the case of specific chemical compounds, is used *exclusively* for alcohols, and when so used is never followed by a final **e**. The last syllable is pronounced **-ōl** (as, glȳ'cōl, phē'nōl, crē'sōl, thȳ'mōl (ti), glў'cerōl, quĭ'nōl). Exceptions: ălcohŏl, a'rgŏl.

Terminations in -ole.—This termination is always pronounced **-ōle**, and its use is limited to compounds which are not alcohols (as, ĭ'ndōle).

Terminations in -yl.—No final **e** is used; the syllable is pronounced **ȳl** (as, ă'cetўl, ă'mўl, cē'rotўl, cē'tўl, ĕ'thўl).

Terminations in -yde.—The **y** is long (as, ă'ldehȳde).

Terminations in -meter.—The accent follows the general rule (as, hydrŏ'meter, barŏ'meter, lactŏ'meter). Exception: words of this class used in the metric system are regarded as compound words, and each portion retains its own accent (as, cĕ'ntime''ter, mi'llime''ter, kĭ'lome''ter).

Miscellaneous Words which do not fall under the preceding rules.

Note the spelling:

albumen
albuminous
albuminiferous
asbestos
gramme
radical

Note the pronunciation:

a′lkalīne
a′lloy (n. & v.)
a′llotropy
a′llotropism
ī′somerism
pŏ′lymerism
apparā′tus (sing. & plu.)
āqua regia
barȳ′ta
cĕntigrade
co′ncentrated
crystallĭn or crystallīne
electrŏ′lysis
lîter
mŏ′lecule
mŏlĕ′cular
nō′menclā″ture
olē′fiant
vā′lence
ū′nivā″lent
bī′vā″lent
trī′vā″lent
qua′drivā″lent
tĭ′trate

A List of Words whose Use should be Avoided in Favor of the Accompanying Synonyms.—

For	*Use*
sodic, calcic, zincic, nickelic, etc., chlorid, etc.	sodium, calcium, zinc, nickel, etc., chlorid, etc. (*vide* terminations in -ic, *supra*).
arsenetted hydrogen	arsin
antimonetted hydrogen	stibin
phosphoretted hydrogen	phosphin
sulfuretted hydrogen, etc.	hydrogen sulfid, etc.
beryllium	glucinum
niobium	columbium
glycerin	glycerol
hydroquinone (and hydrochinon)	quinol
pyrocatechin	catechol
resorcin, etc	resorcinol, etc.
mannite	mannitol
dulcite, etc	dulcitol, etc.
benzol	benzene
toluol, etc	toluene, etc.
thein	caffein
furfurol	furfuraldehyde
fucusol	fucusaldehyde

For	*Use*
anisol	methyl phenate
phenetol	ethyl phenate
anethol	methyl allylphenol
alkylo′gens	alkyl haloids
titer (n.)	strength or standard
titer (v.)	titrate
monovalent	univalent
divalent, etc	bivalent, etc.
quantivalence	valence

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marîne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, y̆ = ĭ.

′ Primary accent; ″ secondary accent.

N.B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

CHAPTER IV.

ATOMS, ATOMIC MASS, VALENCE.

Introductory.—Lavoisier was the first to recognize the fact that the elements combine in definite mass-proportions.

Proust, another French chemist, was the first to prove that the elements combine in a small number of definite fixed proportions, but he did not succeed in giving a correct explanation of chemical combination.

John Dalton's investigations led him, independently of the work of others, to the discovery of the law of combination in multiple proportions.

Laws of Chemical Combination.—The two important laws of chemical combination can be thus stated:

LAW OF DEFINITE PROPORTIONS: Chemical combination always takes place between definite masses (weights) of substances.

LAW OF MULTIPLE PROPORTIONS: If two elements combine in different proportions, the relative amounts of the one which combine with a fixed amount of the other are simple multiples of each other. In order to explain these facts, Dalton advanced his famous Atomic Theory.

Two hypotheses concerning the constitution of all elementary forms of matter present themselves for consideration.

Matter is either infinitely divisible, or it is not infinitely divisible.

Concerning the former hypothesis this, from its very nature, is incapable of direct proof or demonstration, and must always remain solely a subject for speculation.

Acceptance of the second hypothesis involves of necessity the assumption of the existence of ultimate, indivisible particles of matter. Such particles are termed atoms, from the Greek *ατομος*, signifying indivisible.

Dalton conceived the idea that there might be some connection between the laws of fixed and multiple proportions, and the hypothesis that matter consists of indivisible particles, atoms.

Atomic Mass.—One universal property of matter is mass (weight). As atoms are assumed to be the ultimate particles of matter, atoms must be possessed of mass (weight).

As the different fundamental forms of matter, the so-called elements, differ from one another in their mass, it is only reasonable to suppose that the very atoms of the elements differ from one another in this respect.

It is assumed whenever chemical combination occurs between two elements, that the union takes place between the atoms of these elements.

In case an equal number of atoms of two elements, *A* and *B*, are allowed to enter into chemical combination, a new substance will be formed as the result of such union, and, providing that said elements combine with each other atom for atom, no trace will be left of either of the constituents *A* and *B*.

If the mass of an atom of *A* is 1, and the mass of an atom of *B* is 15, then, as *A* and *B* are supposed to combine atom for atom, the resulting compound would contain *A* and *B* in the proportion of one part by weight of *A* to fifteen parts by weight of *B*.

If therefore, on analysis, a compound is found to contain one part by weight of one element to, say, fifteen parts by weight of another, the inference might be drawn that the masses of the atoms of these elements bear to each other the ratio of 1: 15, an inference which does not necessarily follow.

Assuming matter to consist of atoms, and assuming chemical action to take place between atoms, it is evident why chemical action always takes place between definite amounts by weight, and there is thus gained a feasible explanation of the law of combination in definite proportions.

Furthermore, it follows, as atoms are indivisible, that if elements combine with one another in more than one proportion, the proportions in which they combine must necessarily be a very simple one; for instance, as 1 : 1, as 1 : 2, as 1 : 3, and so on.

This would fully explain the law of combination in multiple proportions.

Standards of Atomic Mass.—The atom is the smallest mass of an element which can enter into chemical combination.

The atomic mass of an element is the relative mass of an atom of that element, referred to the mass of an atom of some other element taken as unity.

The selection of an element as standard of atomic mass presents considerable difficulty.

Hydrogen was selected by Dalton as his standard, and it is the unit of atomic masses still generally used, because hydrogen enters into chemical combinations in smaller proportion by weight than any other element.

Berzelius adopted oxygen as standard, calling $O = 100$.

As the atomic masses of many elements can be determined directly with reference to oxygen, some eminent chemists have lately again urged the adoption of oxygen as the standard, making $O = 16$. This would assign to hydrogen an atomic mass of from 1.003 (Ostwald) to 1.007 (Clarke), according to some of the most recent and exact investigations.

The atomic mass values in the first column, with $O = 16$, are taken from a table revised by F. W. Clarke, October, 1891; the values in the second column, with $H = 1$, are taken from A. Rössing, Einführung in das Studium der theoretischen Chemie, 1890.

Table of Atomic Masses.

Name.	Symbol.	Atomic Mass, O = 16.	Atomic Mass, H = 1.
Aluminum	Al	27.	27.04
Antimony	Sb	120.	119.6
Arsenic	As	75.	74.9
Barium	Ba	137.	136.9
Bismuth	Bi	208.9	207.3
Boron	B	11.	10.9
Bromine	Br	79.95	79.75
Cadmium	Cd	112.	111.7
Cæsium	Cs	132.9	132.7
Calcium	Ca	40.	39.91
Carbon	C	12.	11.97
Cerium	Ce	140.2	139.9
Chlorine	Cl	35.45	35.37
Chromium	Cr	52.1	52.4
Cobalt	Co	59.	58.6
Columbium	Cb	94.	93.7
Copper	Cu	63.6	63.18
Erbium	Er	166.3	166.
Fluorine	F	19.	19.1
Gadolinium	Gd	156.1	......
Gallium	Ga	69.	69.9
Germanium	Ge	72.3	72.3
Glucinum	Gl	9.	9.08
Gold	Au	197.3	196.7
Hydrogen	H	1.007	1.
Indium	In	113.7	113.6
Iodine	I	126.85	126.54
Iridium	Ir	193.1	192.5
Iron	Fe	56.	55.88
Lanthanum	La	138.2	138.0
Lead	Pb	206.95	206.4
Lithium	Li	7.02	7.01
Magnesium	Mg	24.3	24.30
Manganese	Mn	55.	54.8
Mercury	Hg	200.	199.8
Molybdenum	Mo	96.	95.9
Neodymium	Nd	140.5	......
Nickel	Ni	58.7	58.6
Nitrogen	N	14.03	14.01
Osmium	Os	190.8	191.
Oxygen	O	16.	15.96
Palladium	Pd	106.6	106.2

TABLE OF ATOMIC MASSES.—*Continued.*

Name.	Symbol.	Atomic Mass, O = 16.	Atomic Mass, H = 1.
Phosphorus	P	31.	30.96
Platinum	Pt	195.	194.3
Potassium	K	39.11	39.03
Praseodymium	Pr	143.5	......
Rhodium	Rh	103.	104.1
Rubidium	Rb	85.5	85.2
Ruthenium	Ru	101.6	103.5
Samarium	Sm	150.	150.
Scandium	Sc	44.	43.97
Selenium	Se	79.	79.0
Silicon	Si	28.4	28.3
Silver	Ag	107.92	107.66
Sodium	Na	23.05	23.0
Strontium	Sr	87.6	87.3
Sulphur	S	32.06	31.98
Tantalum	Ta	182.6	182.
Tellurium	Te	125.	125.
Terbium	Tb	160.	......
Thallium	Tl	204.18	203.7
Thorium	Th	232.6	232.0
Thulium	Tu	170.7	......
Tin	Sn	119.	118.8
Titanium	Ti	48.	48.0
Tungsten	W	184.	183.6
Uranium	U	239.6	239.0
Vanadium	V	51.4	51.1
Ytterbium	Yb	173.	172.6
Yttrium	Yt	89.1	88.9
Zinc	Zn	65.3	65.1
Zirconium	Zr	90.6	90.4

It is evident that in many instances the values given in these two tables are based on different sets of data.

If it be desired to learn the atomic mass of any element determined with reference to O = 16, on the basis of H = 1, it will only be necessary to fix on the ratio of O to H, and then a simple calculation by proportion will yield the desired result.

This ratio has been most carefully determined by several observers; following are some of the results obtained.

	H.		O.
Dumas	1	:	15.96
Erdmann, Marchand	1	:	15.96
Cooke, Richards (with Rayleigh's corrections)	1	:	15.869
Keiser	1	:	15.949
Regnault, Rayleigh, Crafts	1	:	15.91
Rayleigh	1	:	15.884

Determination of Atomic Mass.—The determination of the atomic masses of the elements is based on a chemical analysis of their compounds.

It is, however, impossible to ascertain the atomic mass of an element solely from the results of an analysis of its compounds, for atoms cannot be isolated and then be weighed.

If atoms of different elements were to combine with each other in only one proportion, a determination of the relative masses in which these elements are present in compounds, would permit of an inference as to the relative masses of the atoms.

But elements frequently combine with each other in more than one proportion, and therefore, besides ascertaining the relative amounts by weight in which the different elements are present, it is absolutely necessary that the number of atoms constituting a molecule be known.

Direct Determination.—In order to determine the atomic mass of an element, the first step to be taken, is the analysis of all of the compounds of the element with hydrogen, assuming hydrogen to be adopted as the unit of atomic mass, and a comparison of the values found, in order to ascertain the smallest amount by weight of that element which exists in combination with hydrogen.

A few problems will illustrate the method pursued.

EXAMPLES.

a. Required, the atomic mass of chlorine.—

The compound of chlorine with hydrogen is hydrochloric acid. This compound, subjected to most careful analysis, shows that in every 100 parts by weight of hydrochloric, acid there are contained 2.74 parts by weight of hydrogen and 97.26 parts by weight of chlorine.

Making the proportion:

$$2.74 : 97.26 :: 1 : x,$$
$$x = 35.5.$$

This means that, in this compound, the amount of chlorine which combines with unit mass, i.e., with one atom of hydrogen, has a mass 35.5 times as great as that of the hydrogen, and as no compound of hydrogen and chlorine is known which contains less of chlorine by weight than this amount, 35.5 is considered the smallest amount of this element which will enter into chemical combination with hydrogen.

b. Required, the atomic mass of oxygen.—

Oxygen forms two compounds with hydrogen: water and hydrogen peroxide. 100 parts by weight of water consist of 11.112 parts of hydrogen and 88.888 parts of oxygen.

$$11.112 : 88.888 :: 1 : x,$$
$$x = 8.0.$$

This means that, in this compound, 8 parts by weight of oxygen unite with 1 part by weight of hydrogen.

100 parts of hydrogen peroxide consist of 5.882 parts of hydrogen and 94.118 parts of oxygen.

$$5.882 : 94.118 :: 1 : x,$$
$$x = 16.0.$$

This means that, in this compound, 16 parts by weight of oxygen unite with 1 part by weight of hydrogen, and as no other compounds of oxygen with hydrogen are known, besides these two here considered, i.e., water and hydrogen peroxide, it appears, that 8 parts by weight of oxygen, is the smallest amount of this element which enters into chemical combination with 1 part by weight of hydrogen.

The number which expresses the smallest weight of an element which will combine with or replace the unit weight of hydrogen, is called the *chemical equivalent* of that element. The atomic mass must be identical with, or must be a multiple of, this value.

Indirect Determination.—In cases where the element, the atomic mass of which is sought, does not form a compound with hydrogen, if that be the unit to which the atomic masses are referred, the atomic mass of the element is determined indirectly, that is, with reference to some other element, the atomic mass of which has been directly determined. The atomic masses of many, if not of most, of the elements have been determined in this manner.

EXAMPLE: 100 parts of sodium chloride consist of 60.68 parts of chlorine and 39.32 parts of sodium.

As 35.5 parts of chlorine combine with 1 part of hydrogen, the amount of sodium which combines with 35.5 parts of chlorine represents the atomic mass of the sodium.

$$60.68 : 39.32 :: 35.5 : x,$$
$$x = 23.$$

Therefore the atomic mass of sodium is 23, of course, on the supposition that the molecule of sodium chloride consists of only one atom of chlorine and one atom of sodium.

When the relative mass of an element in combination with one atom of hydrogen has been thus determined, directly or indirectly, there remain to be ascertained the number of hydrogen atoms in the compound; the mass of the other constituent, combined with these hydrogen atoms, represents the total atomic mass of that element.

Aids in Determining Atomic Mass: Vapor Density.—When the compounds analyzed can be vaporized without decomposition, a determination of the vapor density affords the means of determining their molecular mass. The weights of equal volumes of gases bear to one another the same ratio as the atomic masses of those elements.* Thus,

1 litre of	hydrogen	weighs	0.0896 gramme.
1 " "	nitrogen	"	1.2544 grammes.
1 " "	oxygen	"	1.4336 "

---

* Excepting mercury, cadmium, zinc, phosphorus, and arsenic.

The ratio of the atomic masses of these elements is practically the same as that shown by the figures, viz., 1 : 14 : 16.

According to the hypothesis of Avogadro, "equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules." As before stated, the weights of equal volumes of gases are readily determined; these weights bear the same relation to each other as do the masses of the molecules of these substances; hence it follows, that the molecular mass of all substances is directly proportional to the specific gravity of these substances in the state of a perfect gas.

Under the standard conditions of temperature and pressure, one litre of hydrogen weighs 0.0896 gramme, and one litre of hydrochloric acid gas weighs 1.6352 grammes. The weight of a molecule of hydrochloric acid must therefore be $\frac{16352}{896} =$ 18.25 times as great as that of a molecule of hydrogen.

18.25 parts by weight of hydrochloric acid gas consist of 0.5 of hydrogen combined with 17.75 of chlorine. Therefore 36.5, that is, 18.25×2, contains unit weight of hydrogen, and hence is the smallest number that can be adopted as the molecular mass of hydrochloric acid.

As seen above, the molecule of hydrochloric acid is 18.25 times as heavy as that of hydrogen; therefore, if the atom of hydrogen is 1, the molecular mass of hydrogen must be $\frac{36.50}{18.25} = 2$.

The *atom* of hydrogen is the unit of the atomic masses, and the *molecule* of hydrogen, consisting of two atoms, has been adopted as the standard for the specific gravity of gases. Hence, the molecular mass of any substance is equal to *twice* its specific gravity in the state of gas.

To return to two of the examples previously given, those referring to hydrochloric acid and to water.

As the molecular mass of every substance is the sum of its atomic masses, the values obtained by analysis—the combining masses—must, when added together, result in either the molecular mass, or in a number of which the molecular mass is a multiple.

Analysis has shown, that for every 1 part by weight of hydrogen in hydrochloric acid there are 35.5 parts by weight of chlorine. Hence $1 + 35.5 = 36.5$ is the molecular mass of hydrochloric acid, or if not, then the molecular mass of hydrochloric acid must be some multiple of this value.

The vapor density of hydrochloric acid is found to be 18.25. As the molecular mass of a substance is equal to twice its vapor density, $18.25 \times 2 = 36.5$ must be the molecular mass of hydrochloric acid, as previously stated. But this is also the value found by analysis; therefore hydrochloric acid must consist of one atom of hydrogen and one atom of chlorine, and the atomic mass of chlorine must therefore be $36.5 - 1.0 = 35.5$.

Now, turning to the other example. Analysis of water shows that 1 part by weight of hydrogen combines with 8 parts by weight of oxygen. $1 + 8 = 9$; therefore 9 must be the molecular mass of water, or else the molecular mass of water must be some multiple of this value.

The vapor density of water is $= 9$. The molecular mass of water is therefore equal to $9 \times 2 = 18$.

The combining masses of hydrogen and of oxygen in water were, by analysis, found to be respectively 1 and 8. But the molecular mass was found to be twice this value, that is, 18, and therefore a molecule of water must contain twice as much of each constituent, that is to say, 2 of hydrogen and 16 of oxygen, and the atomic mass of oxygen is therefore 16.*

Atomic Heat.—When the vapor density of an element cannot be obtained, then, in order to fix upon its atomic mass, recourse is often had to the fact discovered by Dulong and Petit in 1819, that the specific heat of an element is inversely proportional to its atomic mass.

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* Assuming the molecule of water to consist of three atoms.

Specific heat is the ratio of the amount of heat required to raise a given weight of a body one degree in temperature, compared to the amount of heat required to raise the same weight of water to the same extent.

The product of the specific heat by the atomic mass is approximately a constant; it is called the atomic heat. Its average value is 6.4, and the atomic mass of an element may therefore be approximately obtained by dividing the specific heat of the element, in the solid state, into 6.4.

EXAMPLE: 100 parts of chloride of silver consist of 75.26 parts of silver and 24.74 parts of chlorine.

As 35.5 parts of chlorine combine with 1 part of hydrogen, the amount of silver which combines with 35.5 parts of chlorine must be the atomic mass of silver.

$$24.74 : 75.26 :: 35.5 : x$$
$$x = 108.$$

Hence the atomic mass of Ag = 108.

To confirm, or to dispose of, the assumption that this value represents the mass of *one* atom of Ag, the constant 6.4 is divided by the specific heat of silver. The specific heat of silver has been ascertained to be 0.057.

$$6.400 : 0.057 = 112.$$

This value 112 is near enough to 108 to show that this represents the mass of *one* atom, and not of several atoms of silver

To a limited extent the principle here referred to can also be extended to chemical compounds, for the specific heat of elements is practically the same when they are in a state of combination, as when they are in a free state.

The molecular mass of a compound, multiplied by its specific heat, is equal to as many times 6.4 as there are atoms in the molecule.

The specific heat of sodium chloride, for instance, is 0.214. Its molecular mass, on the assumption that it consists of one atom of sodium and one atom of chlorine, is $23.0 + 35.5 = 58.5$.

$$58.5 \times 0.214 = 12.52;$$
$$12.52 \div 6.4 = \text{about } 2,$$

thus confirming the view above assumed in regard to the constitution of the molecule of sodium chloride.

Isomorphism.—This property was at one time regarded as a valuable aid in the determination of the atomic mass of elements.

Mitscherlich believed, that isomorphism, which he defined as identity of crystalline form, was due only to the number and the arrangement of the atoms in a molecule, and that it was entirely independent of the chemical nature of these atoms. He taught, that an equal number of atoms united in the same manner, gives the same crystalline form.

This statement, if it were borne out by the facts, would furnish a valuable guide in atomic-mass determinations. For, two compounds being isomorphous, it could be assumed that they contained the same number of atoms in their molecules. Then, knowing the atomic masses of the elements in the molecule of one of these substances, the atomic mass of one element in the other substance could be easily calculated.

However, it can readily be shown that this method does not give reliable results, at least not, if the broad meaning assigned by Mitscherlich to the term isomorphism, be retained.

Valence.—It has been established by experiment that some elements will enter into chemical combination in but one proportion, while other elements will readily enter into combination in more than one proportion.

To account for these facts, the hypothesis has been advanced, that this power of forming combinations is inherent in the atoms.

This property is usually designated as the valence, the valency, atomicity, quantivalence, or the atomic value of the atoms, and the valence of an element is generally expressed by the number of hydrogen atoms, or their chemical equivalent, which one atom of that element can combine with, or replace. Thus:

1 atom of Cl combines with 1 atom of H.
1 " " O " " 2 atoms of H.
1 " " N " " 3 " " "
1 " " C " " 4 " " "
1 " " P " " 5 " " "

From this it is evident that oxygen can exhibit twice, nitrogen three, carbon four, and phosphorus five times, the combining power of the hydrogen atom.

The relation between the chemical equivalent of an element and its atomic mass, is a simple one.

The atomic mass, is either equal to, or it is two, three, four, five, six, seven, or eight times as great as the chemical equivalent.

This relation is expressed by the formula:

$$A = E \times V,$$

where $A =$ atomic mass,
$E =$ chemical equivalent,
$V =$ valence.

Standard of Valence.—The combining power of an atom of hydrogen is usually selected as the unit of valence, and the combining values of the atoms of other elements are expressed in terms of this unit.

When an element can combine with or replace hydrogen, atom for atom, it is termed a monad—from the Greek *μόνος*, one; if an element combines with, or takes the place of, two atoms of hydrogen, it is termed a dyad; if three, a triad; if four, a tetrad; if five, a pentad; if six, a hexad, and so on.

Elements having an odd number of bonds (monads, triads, pentads, heptads), are termed perissads; those having an even number of bonds (dyads, tetrads, hexads, octads), are termed artiads.

Manner of Designating Valence.—The valence of an element is represented by Roman numerals placed above, or by dashes, called bonds, which are placed at the side of the symbol of the element; the number of the dashes indicates the valence. Thus,

$$\mathrm{H}-\qquad \mathrm{O}=\qquad \mathrm{N}\equiv\qquad \mathrm{C}\genfrac{}{}{0pt}{}{=}{=}\qquad \mathrm{P}\genfrac{}{}{0pt}{}{=}{\equiv}$$

indicate that.

H is a monad element,
O " dyad "
N " triad "
C " tetrad "
P " pentad "

Variable Valence.—The position of these bonds is absolutely immaterial, their number only possesses significance.

With but few exceptions the elements can exhibit variations in their valence, and when this is done, the valence is generally varied by two bonds.

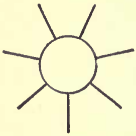
Thus, a monad may be transfomed into a triad or a pentad, while a dyad can be caused to act as a tetrad or a hexad.

In order to account for this, the assumption is made, that when a change in valence takes place, two bonds neutralize each other, as indicated in the figure on page 66.

It certainly seems, that this idea of intra-linkage, that is to say, the union of some of the affinities of an atom with other affinities of the same atom, accounts well for the phenomenon of variable valence.

Based on certain observations concerning the variable valence of nitrogen and of phosphorus, it has been assumed, that valence is a property of atoms dependent upon varying conditions—chiefly upon the temperature. It has been held, that at low temperatures the valence of the elements is greater, while at higher temperatures the valence is decreased. However, there seem to be serious objections to the acceptance of this view.

Owing to the difficulty, not to say impossibility, of determining the true cause of variable valence, Wurtz suggested, that the idea of a fixed valence of the atoms be abandoned, and that the valence exhibited by an atom in any given combination be regarded as the outcome of the attractive forces of all of the atoms in that combination. He believed a knowledge of the valence which an element exhibits in any given compound to be of far greater importance, than all attempts could be, which might be made for the determination of a fixed valence.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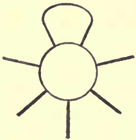
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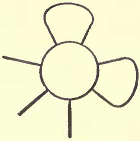
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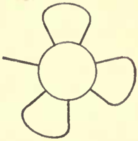
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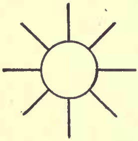
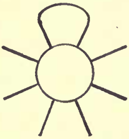

OCTAD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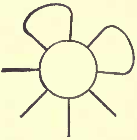
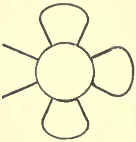

TETRAD


DYAD

Remsen has proposed to designate the valence of an atom in the sense that Wurtz suggested, as the "apparent valence," and to reserve for valence regarded as a fixed property of the atom, the term "true valence."

Determination of Valence.—When elements replace one another in chemical combinations, the number of atoms of the elements taking part in the reaction, depends to a certain extent upon their respective valence.

One atom of a monad element can of course be replaced only by one atom of some other monad element. One atom of a dyad can be replaced by one atom of some other dyad, or by two monad atoms; a triad may be replaced by three monad atoms, or by one dyad and one monad atom, or by some one other triad atom; a tetrad can be replaced by four monad atoms, by two dyad atoms, one triad and one monad, or by one atom of another tetrad element.

The determination of the valence of the elements is therefore an important matter.

If the degree of combining power, the valence, which an atom of hydrogen possesses, be accepted as the unit, then the determination of the valence of those elements which form compounds with hydrogen, and of which the molecular mass can be determined, proves a simple matter.

For instance, in order to determine the valence of oxygen, all compounds of oxygen with hydrogen must be analyzed.

Two such compounds exist, and of these two, water has been found to contain the smallest proportion of oxygen to hydrogen. It is therefore assumed, that in one molecule of water there is but one atom of oxygen.

Analysis has shown that sixteen parts by weight of oxygen are combined with two parts by weight of hydrogen. The atomic mass of oxygen is 16. Therefore, as the smallest amount of oxygen known to exist in chemical combination, an atom of oxygen, is not known to occur in combination with less than two atoms of hydrogen, each of which possesses the valence one, the valence of an atom of oxygen must be two.

Even if no compound of an element with hydrogen is known, the valence of the element referred to the atom of hydrogen as standard, can be ascertained by the indirect method, by the aid of chlorine, bromine, etc., as previously explained in the determination of atomic masses; for this, a knowledge of the molecular mass of the compound is, however, essential.

If elements exhibit variable valence, and, as already stated, nearly all of them do, it is desirable that there should be determined, what might be termed, their minimum and their maximum valence.

By minimum valence is meant the lowest valence which an element is known to exhibit in any combination; and by maximum valence, the highest combining power which it is known to possess.

To ascertain these values, of course an analysis of *all* of the compounds of an element would be necessary. Few elements exhibit more than two powers of valence.

CHAPTER V.

CHEMICAL FORMULÆ.

Introductory.—A molecule may be defined as the smallest particle of matter which can exist uncombined, or, as the smallest quantity of matter in which its properties inhere.

Molecules of the elements consist of atoms of the same kind of matter; molecules of compounds are combinations of atoms of different kinds of matter.

Chemical analysis readily affords answer to the query whether a given substance consists of one or of more than one kind of matter, in other words, whether the molecules of a given substance are composed of atoms of the same, or of various kinds.

Furthermore, chemical analysis permits of the determination of the percentage composition of a compound substance, but when it comes to the assigning of a chemical formula—a chemical formula being the expression in symbols of the chemical constitution of a body—the domain of experimental research no longer affords adequate data, and the aid of theory must be invoked.

Determination of Empirical Formulæ.—The *simplest* expression of the ratio of the atoms in a molecule, is obtained by dividing the percentage amount of each element occurring in the molecule by its atomic mass, and then finding the simplest set of whole numbers which bear to one another the ratio of the quotients found.

These figures represent the relative number of atoms of each constituent present. Thus, for instance, let it be required to ascertain the formula of a substance having the following composition:

Carbon..................	52.18 per cent.
Hydrogen................	13.04 " "
Oxygen..................	34.78 " "

The following calculation will yield the desired result:

$$\begin{array}{ll} \text{C.} & 52.18 \div 12 = 4.35 = 2. + \\ \text{H.} & 13.04 \div 1 = 13.04 = 6. + \\ \text{O.} & 34.78 \div 16 = 2.17 = 1. + \end{array}$$

This shows that the elements carbon, hydrogen, and oxygen are present in the proportion of 2 : 6 : 1, and therefore the simplest formula of this substance would be C_2H_6O.

The ratio in which the atoms forming a compound are present, can be readily determined if the percentage composition of the compound and the specific heat of one of the components be known.

EXAMPLE : Analysis of an oxide of iron showed it to consist of 30 per cent of oxygen and 70 per cent of iron.

Atomic mass of oxygen = 16.
Specific heat of iron = 0.114.
$6.4 \div 0.114 = 56. +$

Hence 56. is *approximately* the atomic mass of the iron.

Assuming that there is present in the molecule at least one atom of Fe, and of course there can be no less, then:

$$70 : 30 :: 56 : 16x.$$
$$x = 1.5.$$

This means that for every atom of iron in the molecule there are present $1\frac{1}{2}$ atoms of oxygen. But as half-atoms cannot exist, the atoms of Fe and the O are present in the proportion of 2 : 3.

Of course this proceeding gives only approximately correct results, as allowance must always be made for experimental errors and inaccuracies.

The formula expressing simply the ratio in which the elements forming a compound, are present, is termed the empirical formula of the substance. Such a formula, although exhibiting the ratio in which the different elements forming a substance are present, leaves its actual constitution undetermined.

Determination of Molecular Formulæ.—A molecular formula is intended to indicate the number of atoms of each of the elements in a molecule, as well as to show the mere numerical ratio obtaining between them. The molecular formula of a substance may therefore be identical with, or a multiple of, the empirical formula of that substance.

In order to determine the correct molecular formula of a body, the molecular mass of the substance must be known, when a simple calculation will yield the desired result.

Thus, for instance, if the percentage composition of a substance be given as:

Carbon	52.18
Hydrogen	13.04
Oxygen	34.78

and the molecular mass as 46, then the molecular formula would be calculated as follows:

C. $100 : 52.18 :: 46 : x = 24$, total atomic mass of the carbon.
H. $100 : 13.04 :: 46 : x = 6$, “ “ “ “ “ hydrogen.
O. $100 : 34.78 :: 46 : x = 16$, “ “ “ “ “ oxygen.

As the atomic masses of carbon, hydrogen, and oxygen are respectively 12, 1, and 16,

$\frac{24}{12} = 2$, the number of atoms of C in 1 molecule.

$\frac{6}{1} = 6$, “ “ “ “ “ H “ “ “

$\frac{16}{16} = 1$, “ “ “ “ “ O “ “ “

and the molecular formula of this substance is, therefore, C_2H_6O.

There are several methods of determining the molecular mass of substances.

Determination of Molecular Mass: Method of Chemical Analysis.—This method can be resorted to in all cases. It involves a study of the chemical behavior of the body under consideration, an analysis of its compounds and derivatives, and the drawing of certain conclusions from the results thus obtained.

This method of procedure can best be illustrated by an example. Suppose it were required to determine the molecular mass of nitric acid. Analysis of numerous salts of this acid show it to be monobasic, that is to say, show that it contains but one atom of hydrogen which is replaceable by metals.

This having been ascertained, careful analysis is made of the nitric acid salt of some metal, the atomic mass of which has been accurately established. Nitrate of silver answers this purpose well. This compound contains 63.53 per cent of silver.

Making the proportion:

$$100 : 63.53 :: x : 108,$$
$$x = 170.$$

That is, the molecular mass of nitrate of silver is 170. But this compound differs from nitric acid in having one atom of silver in the place of one atom of hydrogen;

therefore, 170
minus 108, the atomic mass of silver,

is 62, and this
plus 1, the atomic mass of hydrogen,

equals 63, the molecular mass of nitric acid, the value sought.

Method of Vapor-Density Determination.—This method is applicable only to those substances which can be transformed into the gaseous condition without suffering decomposition.

As stated in the previous chapter, equal volumes of all gases and vapors, under the same conditions of temperature and pressure, contain an equal number of molecules.

The specific gravity of gases and vapors is referred to $H. = 1.0$; molecular weights are referred to $H_2 = 2.0$. The molecular mass of a substance is therefore obtained by multiplying the specific gravity of its vapor referred to hydrogen, by 2.

In case that the specific gravity of a substance in the gaseous condition has been referred to air $= 1.0$, then its molecular mass is ascertained by multiplying this specific gravity value by 2×14.43, that is, by 28.86, for the specific gravity of air referred to hydrogen is 14.43.

The different methods used in making determinations of the vapor density of a substance have previously been fully discussed, and may be referred to again in this connection.*

Methods based on Properties of Substances when in Solution.—The principal methods which call for consideration under this heading rest, respectively, on the determination of the osmotic pressure, on the lowering of the vapor-pressure, on the rise of the boiling-point, and on the depression of the freezing-point of solutions.

METHOD A. *Osmotic Pressure.*—Substances when brought into a state of dilute solution exhibit in their behavior a marked resemblance to their deportment when in the gaseous condition.

Experience has taught, that the particles of a substance when in dilute solution exercise a pressure, called the osmotic pressure, which is equal to the pressure that would be exerted by the same amount of the substance if the solvent were removed, and the substance, transformed into a gas, were, at the same temperature, made to occupy the same volume previously filled by the solution.

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* Chapter II.

This fact, as formulated by Van 't Hoff, is thus stated: The osmotic pressure in a solution, like the tension of a gas, is independent of the nature of the molecules, but is directly proportional to their number, and is equal to the corresponding tension exercised by the body in the gaseous state.

The osmotic pressure method, therefore, affords a means of indirectly determining vapor-densities, and from these, of course, the molecular masses can readily be calculated by aid of Avogadro's law.

The experimental difficulties of making direct determinations of osmotic pressure are very great, and such determinations are therefore but rarely made. There are, however, several serviceable methods which permit of an indirect determination of the osmotic pressure, and as the lowering of the vapor-tension and the lowering of the freezing-point of solutions are proportional to their osmotic pressure, measurements of this character are made use of for the determination of molecular mass.

METHOD B. *Lowering of the Vapor-pressure.*—The vapor-pressure of a solvent is lowered by the addition of a non-volatile substance. This lowering of the vapor-pressure is proportional to the quantity of the substance dissolved, and is equal to the number of the molecules dissolved, divided by the number of molecules of the solvent.

Basing on this fact, the molecular mass of a substance can be ascertained, after securing the experimental data necessary, by the formula:

$$M = M_0 \frac{mp'}{100(p - p')};$$

where, M = molecular mass of the substance dissolved;
M_0 = " " " solvent—ascertained by a vapor-density determination;
p = vapor-pressure of the pure solvent at any given temperature;

p' = vapor-pressure of a solution in which for each 100 grammes of solvent, there are m grammes of dissolved substance.

But as the experimental difficulties to be overcome in this method are also very great, its application also is but limited.

METHOD C. *Elevation of the Boiling-point.*—This method, due to Beckmann, is comparatively simple and furnishes reliable results. Originally it was intended to be used only in determinations where the dissolved substance was non-volatile, but it has lately been so extended by Nernst that it can now also be applied in the case of volatile substances.

Determinations by this method are made in a glass flask provided with a condenser and furnished with a thermometer very accurately graduated. The supply of heat is carefully regulated, and is generally transmitted to the liquid by means of a platinum wire fused into the apparatus.

When the temperature of the boiling solution has become constant, a weighed quantity of the substance to be dissolved is introduced, and the elevation of the boiling-point caused thereby, is noted.

Calculation of the molecular mass is effected by the formula:

$$M = E\frac{m}{t};$$

where M = molecular mass of the dissolved substance;
m = as in the previous method;
t = observed elevation of boiling-point;
E = molecular elevation of boiling-point, calculated from the heat of vaporization of 1 gramme of the solvent and its boiling-point, in absolute degrees of temperature.

METHOD D. *Depression of the Freezing-point.*—The freezing-point of solvents is lowered when substances are dissolved in them, and this lowering of the freezing-point takes place according to a law which Raoult first believed could be stated:

The molecular mass of any substance, on dissolving in 100 times the molecular mass of any solvent, lowers the freezing-point of the solvent by very nearly 0.63° C.

Later investigations, however, have shown that this statement is not universally true, and this formulation of the law had therefore to be abandoned.

Let:

A = the coefficient of lowering of the temperature of solidification, that is, the depression of the freezing-point produced by the solution of 1.0 gramme of substance in 100.0 grammes of the solvent;

T = the molecular coefficient of lowering, that is, the depression of the freezing-point produced by the solution of one gramme-molecule (the molecular mass in grammes), of the substance, in 100 grammes of the solvent;

M = the molecular mass of the dissolved substance.

Then,

$$T = MA,$$

and,

$$M = \frac{T}{A}.$$

The value of T is ascertained for each solvent, by direct experiment—by determining the depression of the freezing-point which is produced by substances, the molecular mass of which is known.

The value of A is found by determining the freezing-point of the solvent, first without, and then after introduction of the substance to be dissolved.

Then, if:

P = weight of the solvent;

P' = weight of the dissolved substance;

K = the lowering of the freezing-point produced in the experiment;

$$A = K\frac{P}{P' \times 100}.$$

The mean value of T, as determined by numerous experiperiments, is, for:

Acetic acid = 38.6;
Formic acid = 28.0;
Benzene = 49.0;
Nitrobenzene = 70.5;

$$\text{Water} = \begin{cases} 18.5 \text{ (for organic substances, some salts of dyad metals, all the feeble bases and acids);} \\ 37.0 \text{ (for alkaline and alkaline earthy salts, and for all the strong acids and bases).} \end{cases}$$

The following problem will show the manner of effecting molecular mass determinations by the Raoult method.

EXAMPLE: Determine the molecular mass of propionic acid.

The freezing-point of a sample of acetic acid was found to be 16.490° C. Taking 62.014 grammes of this acid and adding to it 0.2540 gramme of pure propionic acid, the solidifying point of the mixture was found to be 16.277° C. The value of T for acetic acid = 38.6.

The lowering of the freezing-point is:

$$\begin{array}{rl} & 16.490^\circ \text{ C.} \\ \text{less} & \underline{16.277^\circ \text{ C.}} \end{array}$$

$$K = 0.213^\circ \text{ C.}$$
$$P = 62.014 \text{ grammes.}$$
$$P' = 0.254 \quad \text{''}$$

As:

$$A = K \times \frac{P}{P' \times 100}$$

$$A = 0.213 \frac{62.014}{0.254 \times 100}$$

$$A = 0.5199,$$

and as the molecular mass of the dissolved substance is calculated by the formula:

$$M = \frac{T}{A}$$

in this instance:

$$M = \frac{38.6}{0.5199} = 74.2$$

while the calculated molecular mass of propionic acid, C_2H_5COOH, is 74.

CHAPTER VI.

THE STRUCTURE OF MOLECULES.

Introductory.—In order to gain an idea of the manner in which the atoms are grouped to form a molecule of any substance, this substance must be submitted to an exhaustive examination.

If feasible, physical as well as chemical methods must be employed, with a view to gleaning all information possible, regarding the behavior of this substance under the most varied conditions.

Let it be required, for instance, to study a compound of carbon, hydrogen, and oxygen, with the purpose of gaining an insight into its structural condition, in order that a proper formula may be assigned to it.

The information first sought for in such a problem would probably be concerning the behavior of the atoms of the different constituents: whether, for instance, all the atoms of an element behave alike, or whether a difference in their behavior could be determined. In the case of hydrogen, the question would be, whether its atoms may all be replaced by a metal, or all by a non-metal, or whether they are replaceable in part by the one and in part by the other.

As regards the oxygen atoms, attempts would be made to ascertain (by making substitution-products), whether some of these atoms, and if so, what number, are united respectively to the carbon and to the hydrogen atoms; this would permit an inference as to how many groups of hydroxyl (OH) and of carbonyl (CO) exist in the molecule.

Endeavors would be made to prepare the compound in question by synthesis, with a view to gaining further information concerning the grouping of the component elements. Finally, the valence of the elements forming the compound would be carefully considered, so that, in the light of the knowledge obtained with regard to their grouping, a formula might be devised in which due regard would be paid to the valence of the different constituents.

In studying the physical properties of solids and liquids with a view of ascertaining the structure of their molecules, due attention must be given to the subjects of molecular volumes and molecular refraction, as well as to the action which such substances may exercise on polarized light.

Molecular Volume.—This term is applied to the quotient obtained by dividing the molecular mass of a substance by its specific gravity, when in the liquid state and at the boiling point of the liquid, under a pressure of 760 mm.

The determination of the molecular volume is a matter of importance chiefly with organic compounds.

An intimate relation exists between the constitution of substances and their molecular volumes.

Thus, in the following series of organic acids,

Formic,	$H.COOH$,
Acetic,	$CH_3.COOH$,
Propionic,	$C_2H_5.COOH$,
Butyric,	$C_3H_7.COOH$,

each member differs from the preceding member of the series by CH_2. If the molecular volumes of these acids be calculated, it will be found that the molecular volume of each member of this series differs from the preceding member of the series by the constant 22. The conclusion therefore seems justified, that the molecular volume of CH_2 is equal to 22.

From a great number of observations, Kopp, the pioneer in this field of research, deduced a series of values for the specific volumes of the elements when in combination, and in certain classes of compounds.

C = 11.0.
H = 5.5.
O = 12.2 when united to one element by both bonds.
O = 7.8 “ “ “ “ “ “ one bond.
S = 28.6 “ “ “ “ “ “ both bonds.
S = 22.6 “ “ “ “ “ “ one bond.
Cl = 22.8.
Br = 27.8.
I = 37.5.
N = 2.3 (in compounds of the ammonia type).

A knowledge of these data will often permit an inference as to the probable grouping of certain elements in a molecule.

Thus, the molecular volume of acetone, at its boiling-point, is found to be 77.5. Calculating the molecular volume of acetone by aid of the figures just given,

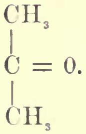
$$\begin{array}{lcr}
C = 3 \times 11 & = & 33.0 \\
H = 6 \times 5.5 & = & 33.0 \\
O = 1 \times 12.2 & = & 12.2 \\
\hline
 & & 78.2
\end{array}$$

the result would be 78.2, assuming that in this substance the oxygen atom is united by both bonds to one element.

If the oxygen atom were united to one element by but one bond, the result would be different, namely:

$$\begin{array}{lcr}
C = 3 \times 11 & = & 33.0 \\
H = 6 \times 5.5 & = & 33.0 \\
O = 1 \times 7.8 & = & 7.8 \\
\hline
 & & 73.8
\end{array}$$

The former figure evidently agrees far more closely with the observed value than the latter, and the constitution of the acetone molecule is therefore assumed to be indicated by the following structural formula:



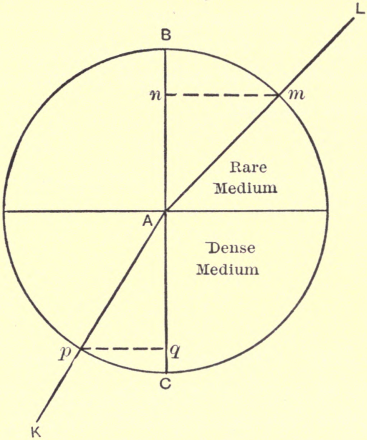
$$\begin{array}{l} CH_3 \\ | \\ C = O. \\ | \\ CH_3 \end{array}$$

Attempts to draw conclusions with regard to the molecular structure of solid substances, from their molecular volumes, has shown that isomorphous compounds, that is to say, compounds which have an analogous composition and which crystallize in the same form, have molecular volumes which are equal or nearly equal.

Thus, the molecular volumes of the sulphates of calcium, barium, and strontium, which constitute an isomorphous group, range from 45.3 to 51.4, and the sulphates of magnesium, zinc, nickel, cobalt, and iron, each crystallized with seven molecules of water, all have their molecular volumes ranging between 145.5 and 147.5.

Molecular Refraction.—When a ray of light passes from one medium into another which is more dense, the ray is bent out of its course and is deflected towards a line conceived at right angles, i.e., perpendicular, to the surface of the more dense medium.

If a circle be drawn from *A* as centre, with a radius equal to unity, and if from the points *m* and *p*, where the circle cuts the incident and the refracted ray, the lines *mn* and *pq* be drawn perpendicular to *BC*, *mn* is called the sine of the angle of incidence, *LAB*, and *pq* the sine of the angle of refraction. *KAC*.



The ratio between the sines of the angle of incidence and of refraction, is termed the index of refraction.

It has been found that an intimate relation exists between the refracting power of certain substances and their constitution.

The specific refractive power of a substance is expressed by the formula:

$$\frac{n-1}{d},$$

where n is the index of refraction, and d is the specific gravity of the substance.

This expression does not hold strictly good for the same substance when in different states of aggregation; thus, for water in the liquid state, the specific refractive power, calculated by above formula, is equal to 0.3338, while for steam, it is equal to 0.3101.

A formula advanced at about the same time, but independently, by Lorenz of Copenhagen and by Lorentz in

Leyden, in the year 1880, yields results much more satisfactory in this respect.

This formula, expressing the refraction-equivalent, is:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d},$$

and gives, for instance, for liquid water the value 0.2061, for steam, 0.2068, values that are almost identical.

If the molecular mass of a substance is multiplied by its refraction-equivalent, thus:

$$m \times \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d},$$

the resulting product is termed the molecular refraction-equivalent of the substance, and represents the specific refracting power of the molecule.

In general, this specific refracting power of the molecule has been found to be equal to the sum of the refractive powers of the atoms of which the molecule consists.

The refraction-equivalent of several kinds of atoms has been carefully determined, notably by Brühl and by Landolt, by the comparing of two compounds which differed from one another by only one or two atoms of the element investigated. These researches have been conducted principally on organic substances, and several interesting and important relations have been traced.

Thus, Brühl found, that all substances in which the presence of doubly-linked carbon atoms was assumed, always possessed a molecular refractive power actually greater than was indicated by calculation from the refractive powers of the atoms, a fact which has proved of value in determining the molecular structure of some compounds.

Thus, for instance, the molecular refraction of benzol is calculated to be:

Carbon (single linkage)	$2.365 \times 6 = 14.190$
Hydrogen	$1.103 \times 6 = 6.618$
Double linking of carbon	$1.836 \times 3 = 5.508$

Calculated molecular refraction = 26.316

Actual observation of n and d leads to the molecular refraction value 25.93; this shows a fairly close agreement, and confirms the customary structural formula assigned to this substance.

Magnetic Rotation of the Plane of Polarized Light.—In 1846 it was discovered by Faraday, that transparent substances, when they are surrounded by a wire through which an electric current flows, or when they are placed in a magnetic field, become capable of rotating the plane of polarized light.

Since 1882 W. H. Perkins has undertaken to investigate the relations existing between the amount of rotation produced and the chemical constitution of the substances producing such rotation. Through his researches it has been learned, that the extent to which rotation is effected, depends upon the nature of the substance, upon the thickness of the section traversed by the light, upon the temperature, and upon the intensity of the magnetic field. Homologous series exhibit an additive character in this property; thus, for instance, it has been found that every CH_2 group produces an increase of 1.023 units.

This power of rotating the plane of polarized light is of some value in determining the class of compounds to which a body belongs. Relations are here found to exist, similar to those, that were noticed in discussing the bearing which the constitution of substances exercises on their molecular refraction power.

Isomerism.—When two compounds have the same percentage composition and identical molecular masses, but exhibit different properties, the compounds are said to be isomeric.

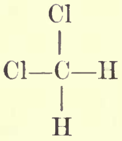
When their percentage composition is the same, but when the molecular mass of the one is a simple multiple of the molecular mass of the other, the compounds are said to be polymeric.

The difference in the behavior of isomeric bodies may be exhibited in their chemical, their physical, and their optical properties.

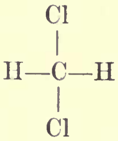
Such differences of properties were already at an early date assumed to be owing to some variation in the arrangement, the grouping, of the atoms constituting the molecules; however all atoms were conceived of as lying in one plane. The study of isomerism dates back to 1824, from which time, until 1873, this view with regard to the nature of isomerism was held.

Stereochemistry.—Wislicenus in the year last named, after an exhaustive study of the grouping of the carbon, hydrogen, and oxygen atoms existent in lactic and in sarcolactic acids, announced the structural identity of these bodies, and stated that the difference between isomeric molecules which have the same structural formula, can only be explained by assuming that such molecules differ from one another by the arrangement, the grouping, of their atoms in space.

If two atoms of hydrogen in CH_4 are replaced by two other monad atoms, for instance by chlorine, then, if the atoms are conceived as grouped in one plane, two isomers are possible, as shown by the following figure:



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl—C—H} \\ | \\ \mathrm{H} \end{array}$$



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{Cl} \end{array}$$

In the one case, the chlorine atoms adjoin one another, in the other they do not.

However, as a matter of fact, only one form of methylene chloride, CH_2Cl_2, is known to exist, and if this view is to be expressed, the atoms must be regarded as grouped in such a manner, that the possibility of isomerism is excluded.

A grouping of this kind is possible only, when the atoms forming the molecule are conceived of as grouped in space, and a form of structure which would meet the requirements is that of a tetrahedron, in which all of the other atoms would hold the same relation to the carbon atom, that the corners of a tetrahedron bear to the centre of the same; then the chlorine atoms, however one may conceive of their being placed, will always adjoin one another.

The theory of the grouping of atoms in space, foreshadowed by Wislicenus, was first distinctly advanced by Van't Hoff in September, 1874, and, independently, by Le Bel, a few months later in the same year.

While the property previously alluded to, of rotating polarized light under the influence of magnetism, is quite general, certain substances exist, in which the power of rotating light is inherent, and which do not require the influence of electricity to bring it into play. This has been known for some time; that certain crystalline solids are capable of thus naturally rotating polarized light, was first noticed in the mineral quartz, by Arago in 1811.

Concerning this power in as far as certain crystalline solids possess it, it is believed to be owing to a definite spiral arrangement of their ultimate particles. At least this assumption is made very plausible by the crystallographic properties of such bodies; in fact an optically active body can be artificially constructed, as first shown by Reusch in 1869, by placing a number of mica plates on one another in such a manner that the optical axis of each plate is placed at a certain angle to the optical axis of the plate which it adjoins.

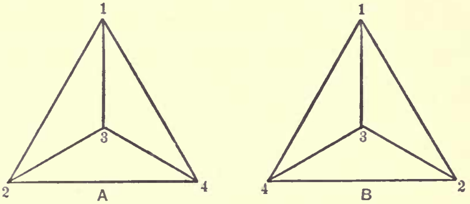
The fact that certain substances in solution will rotate polarized light, was first noticed in sugar solutions by Biot, in 1815. This property of rotating polarized light when in a state of solution, is possessed by quite a number of substances;

these substances are all carbon compounds, and it was with the intention of affording an explanation of these phenomena, that Van't Hoff first advanced his theory.

He assumed that the four valences of the carbon atoms of all such optically active substances are grouped about the carbon atoms in space, and that each one of these valences is united to some atom or radical,—all of the four atoms or radicals being unlike in kind. A carbon atom answering this requirement he denoted as asymmetric.

Van't Hoff's theory affords a plausible explanation of the reason why two isomeric bodies may differ in their optical behavior.

Let 1, 2, 3, 4 denote four different atoms or radicals united to a carbon atom, and let it be assumed that the resulting molecule is represented by the figure of a tetrahedron. Then it will be evident, from the accompanying sketch, that these different atoms or radicals can be grouped about the carbon atoms in such a manner, that the resulting figures, although presenting much similarity, are yet distinctively different and will not admit of superposition.



If now one of these structures possesses the property of rotating a plane of polarized light from left to right, the other structure will rotate it from right to left, for inspection of the above sketch will show, that, in order to pursue the course 1, 2, 4 in figure *A*, one must travel in a direction opposite to the direction in which the hands of a clock move, while in figure *B* the course 1, 2, 4 is traced by moving in the direction followed by the hands of a clock.

Van't Hoff advanced various proofs in support of his theory, and his claims have been most amply confirmed by others. Moreover, it is now regarded as probable that the converse of Van't Hoff's theory is also true, namely, that every asymmetric carbon group is optically active. This, however, must not induce the belief that every substance which contains asymmetric carbon atoms is optically active, for it seems most likely that every compound with asymmetric carbon atoms should exist in two forms, which rotate the plane of polarization to the same degree, but in an opposite sense, and that compounds are possible in which both modifications exist to an equal extent, and which therefore are optically inactive.

Le Bel, who in November, 1874, followed Van't Hoff's announcement with an article bearing on the same subject, was led to his investigations and ultimately to the promulgation of his theory, also by the desire to explain certain optical phenomena displayed by some substances when in solution.

Biot in 1819 and Gernez in 1864 had shown that substances which are optically active when in solution, retain this property when in the vapor form; it therefore seemed probable that this property of affecting polarized light might be a property dependent upon the internal structure of the molecules, and not upon any peculiar arrangement of the molecules themselves. Working upon this supposition Le Bel was led to advance independently the idea that the atoms of such compounds must have a grouping in space, and he was thus brought to share with Van't Hoff the honor of founding the now famous doctrine of stereochemistry.

CHAPTER VII.

CHEMICAL EQUATIONS AND CALCULATIONS.

Definitions.—A *chemical symbol* is the abbreviated designation of an element which represents not only the name of the element, but also the definite proportion by weight in which the element will enter into chemical combination.

Thus, the symbol of chlorine is Cl; the atomic mass of chlorine is 35.5, and this symbol Cl is not only an abbreviated expression of the name of the element, but is to suggest as well the atomic mass of that element, namely, 35.5.

A *chemical formula* is the expression in symbols of the chemical constitution of a compound.

An *empirical* formula is the simplest expression of the ratio in which the elements composing the substance are present; e.g., empirical formula of acetic acid, CH_2O.

A *molecular* formula shows the absolute number of atoms of each of the elements combining to form the molecule, as well as the mere numerical ratio between them; e.g., molecular formula of acetic acid, $C_2H_4O_2$.

A *constitutional* formula aims at illustrating the probable arrangement, the grouping, of the atoms in a molecule.

The molecular formula may, and often does, coincide with the empirical formula; if not, it must be some simple multiple of the latter.

A formula conveys three distinct ideas. It illustrates:

A qualitative relation.

A quantitative relation by weight.

A quantitative relation by gaseous volume.

Thus, the formula NH_3 shows:

First, that NH_3 is a compound of nitrogen and hydrogen.

Secondly, that NH_3 consists of fourteen parts by weight of nitrogen and three parts by weight of hydrogen.

Thirdly, that one volume of nitrogen gas combines with three volumes of hydrogen gas to form two volumes of ammonia gas.

A *chemical equation* is the expression in symbols or formulæ of the changes that elements or compounds undergo when subjected to chemical or, in some instances, to physical influences. As matter is indestructible, these expressions of change must of necessity be equations, for, whatever the change, nothing is lost.

Three kinds of chemical equations may be distinguished: synthetical, analytical, and metathetical.

Synthetical equations are those representing the union of elements or of compounds.

EXAMPLE: $2H + O = H_2O.$
$2KCl + PtCl_4 = K_2PtCl_6.$

Analytical equations illustrate the separation of a compound into its constituents.

EXAMPLE: $CaCO_3 + \text{heat} = CaO + CO_2.$

Metathetical equations demonstrate the interchange of elements or of radicals and the formation of new products.

EXAMPLE: $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$

Some chemists, in the belief of obtaining thereby a more graphic representation of the reactions, prefer the writing of chemical equations in such a manner that the formulæ of the factors taking part are placed in horizontal lines, they being so arranged, that the formulæ of the resulting products appear placed in vertical columns.

Thus, the reaction last given, could be written:

$$\begin{array}{ccc} Ba & & Cl_2 \\ SO_4 & & H_2 \\ BaSO_4 & + & 2HCl \end{array}$$

Metathetical equations—or, as they are also called, equations of interchange—claim attention most frequently, and, in this class, equations of oxidation and reduction present the most interesting problems.*

Oxidizing Agents.—Among the numerous oxidizing agents perhaps the most important are:

	Mode of Action.
Ordinary Oxygen, O_2.	By direct union with a compound.
Ozone, O_3.	By direct union with a compound.
Cl. Br. I.	By direct union with a compound, $2FeCl_2 + Cl_2 = Fe_2Cl_6$, or by combining with the hydrogen of water and liberating oxygen, $2Cl + H_2O = 2HCl + O$.
HNO_3.	$2HNO_3 = H_2O + 2NO + O_3$. Sometimes $= H_2O + 2N + 5O$.
HNO_2.	$2HNO_2 = H_2O + 2NO + O$. Sometimes $= H_2O + 2N + 3O$.
$HClO_3$.	$2HClO_3 = 2HCl + 3O_2$. Or, HCl and various oxides of chlorine.
$HClO$.	$2HClO = 2HCl + O_2$.
H_2SO_4 conc.	$H_2SO_4 + \text{heat} = H_2SO_3 + O = H_2S + 2O_2$.
$H_2Mn_2O_8$ and corresponding salts.	In acid solution: $H_2Mn_2O_8 = H_2O + 2MnO + O_5$. In alkaline solution: $H_2Mn_2O_8 = H_2O + Mn_2O_3 + O_4$. In neutral solution: $H_2Mn_2O_8 = H_2O + Mn_2O_3 + O_4$; or, $H_2Mn_2O_8 = H_2O + 2MnO_2 + O_3$.
H_2CrO_4.	$2H_2CrO_4 = 2H_2O + Cr_2O_3 + O_3$.

Besides these, most of the higher metallic oxides and

---

* Equations of oxidation and reduction are, however, not always metathetical equations.

their compounds can readily act as oxidizing agents. Thus, for instance,

$$\begin{aligned} PbO_2 &= PbO + O, \\ MnO_2 &= MnO + O, \\ Mn_2O_3 &= 2MnO + O. \end{aligned}$$

Reducing Agents.—The chief reducing agents are nascent hydrogen and, as a rule, those compounds of metals which possess a lower quantivalence than the metals can readily assume. Thus, for instance,

$$\begin{aligned} SnO + O &= SnO_2, \\ 2FeO + O &= Fe_2O_3. \end{aligned}$$

Some of the acids readily act as reducing agents, as illustrated by the following:

$$\begin{aligned} H_3PO_2 + O_2 &= H_3PO_4, \\ H_2SO_3 + O &= H_2SO_4, \\ H_2C_2O_4 + O &= H_2O + 2CO_2, \\ H_2S + O &= H_2O + S. \end{aligned}$$

And some hydrides of metals can also exercise this function:

$$\begin{aligned} AsH_3 + O_3 &= H_3AsO_3, \\ PH_3 + O_3 &= H_3PO_3. \end{aligned}$$

Laws of Chemical Interchange.—The laws governing chemical interchange have not yet been fully determined, but it has been found that two conditions exert an important bearing on the result.

1st. Whenever a substance can be formed which is insoluble in the menstruum present, this substance separates as a precipitate.

2d. Whenever a gas can be formed, or any substance which is volatile at the temperature at which the experiment is made, this volatile product is set free.

The law of interchange may also in general terms be stated to be, the tendency to form those substances the formation of which develops the highest thermal effects.

Interchange is always effected on terms regulated by the valence of the elements or radicals involved. That is to say, a monad element or radical can replace another monad element or radical, atom by atom; a dyad element or radical can replace another dyad element or radical atom by atom, while, to effect a similar exchange with monad elements, two atoms of a monad element or radical are needed.

Writing of Chemical Equations: Analytical Method.—Bearing in mind the statements made, to write an equation of interchange, the following simple suggestions may be followed:

1st. Place down as first member of the equation the symbols or formulæ of the substances entering into the reaction, and place the plus sign between them.

2d. Write as terms of the second member of the equation the symbols or formulæ of the products resulting from the reaction.

3d. Adjust the factors of the symbols or formulæ so, that the interchange will result in an equation.

The first step, as given above, needs no comment.

The data for the second step must primarily be determined by actual experiment. In a great many cases, remembering the conditions that affect an interchange and which have been previously stated, there may be predicted, by means of equations, what products will be formed in a chemical metathesis; but it should also be remembered that a chemical equation differs in various ways from an algebraic equation: a chemical equation cannot be accepted as positively true unless verified by experiment; equal amounts cannot be subtracted from either side of a chemical equation, and leave it true, etc.

The third step—the adjusting of the factors—is the important one; and in order the better to illustrate the principles involved, it will be well to work out a few problems in this connection.

EXAMPLE A: Write an equation illustrating that ferrous sulphate is oxidized to ferric sulphate by manganese dioxide, in the presence of sulphuric acid.

In compliance with the directions just given:

$$FeSO_4 + MnO_2 + H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + H_2O.$$

Oxidation signifies an increase in the combining power (the valence) of an element; reduction signifies a decrease in the combining power. Hence an oxidizing agent, in exerting its influence, loses in valence; the substance oxidized experiences a corresponding increase in its valence.

In this instance,

$$\begin{aligned} 2FeO + O &= Fe_2O_3\,, \\ MnO_2 &= MnO + O; \end{aligned}$$

hence the factor for $FeSO_4$ in the above equation is 2, and the factor for MnO_2 is 1.

The presence of free sulphuric acid is indicated by the conditions of the problem.

Therefore, the desired equation will be:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$$

It remains to be seen whether the equation balances. This is easily determined by writing down in a column all the factors and elements that enter into the left hand side of the equation, and checking them off against those of the right-hand member, arranged in like manner.

EXAMPLE B: Construct an equation showing the oxidation of ferrous sulphate to ferric sulphate by potassium permanganate.

This reaction is carried out when it is desired to standardize a solution of potassium permanganate by means of iron.

The operation is as follows:

In an appropriate flask 0.2 gramme of pure iron wire is dissolved in sulphuric acid. Into the resulting solution of ferrous sulphate, there is run a solution of potassium permanganate. The ferrous sulphate is changed to ferric sulphate, i.e., $FeSO_4$ becomes $Fe_2(SO_4)_3$. As long as this reaction continues, the permanganate of potassium solution is decolorized. The instant when all of the $FeSO_4$ has been transformed into $Fe_2(SO_4)_3$ the decomposition of the potassium permanganate ceases, and the solution is no longer decolorized.

The number of cubic centimetres of the potassium permanganate solution used is noted, and this number is divided into the weight of iron taken. The quotient expresses the value, in iron, of one cubic centimetre of potassium permanganate solution.

The substances entering into the reaction to be here considered, are:

$K_2Mn_2O_8$,
$FeSO_4$,
H_2SO_4.

The products resulting are:

$Fe_2(SO_4)_3$,
K_2SO_4,
$MnSO_4$,
H_2O.

Therefore, there should be written,—leaving space for the factors:

$$K_2Mn_2O_8 + FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O.$$

Regarding the change in the valence of the dominant element, the iron in the iron sulphate—auxiliary equations are constructed which show that the iron passes from the dyad to the tetrad state.

$2FeO + O = Fe_2O_3$,
$Mn_2O_7 = 2MnO + 5O$,
Two Fe require one O,
One $K_2Mn_2O_8$ yields five O.

Therefore, 10 of a ferrous compound need 1 of the permanganate.

Hence the quantity of the substance oxidized and the one performing this oxidation must be so adjusted, that the gain in the valence of the former is equivalent to the loss in valence of the latter. Then the factors are arranged for the other substances in accordance with the prescribed conditions of the solution, acid, alkaline, or neutral, and the equation is balanced.

Following these directions, there is obtained:

$$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

and, testing this reaction to see whether it is a true equation:

In first member.		In second member.	
K	2	2	K
Mn	2	2	Mn
O	80	80	O
S	18	18	S
Fe	10	10	Fe
H	16	16	H

The factors all balance, and therefore the equation is correct.

The chief advantage of this method of working out equations of oxidation and reduction, lies in the fact of its insuring a thorough acquaintance with the chemical nature of the changes involved in reactions of this kind.

The Method of Negative Bonds.—A convenient process of constructing equations of oxidation and reduction, is the so-called method of negative bonds.*

A meaning different from the sense in which the word is generally accepted, is assigned to the term bond by this writer. According to him, by the *bond* of an element there is meant the amount of oxidation it is capable of sustaining, and hence his definition of a bond as "oxidizing force," and the statement that, "when an element has no oxidizing force or power, it has no bonds," and that, "when its only capacity is that of a *reducing* agent, its bonds are represented by a negative number."

Among the rules given for ascertaining the number of bonds of an element, are the following:

1. Hydrogen in combination always has one bond, which is always positive (H^{I}).

2. Oxygen always has two bonds, and they are always negative (O^{-II}).

3. Free elements have no bonds; thus, metallic lead (Pb^{0}).

4. The sum of the bonds of any compound is always equal to zero. Thus, $H^{I}N^{+V}O_3{}^{-VI} = 0$.

5. Acid radicals are always negative. Thus,

$$H^{I}I^{V}O_3{}^{-VI} = 0, \text{ or, } Pb_3{}^{VI}(PO_4)_2{}^{-VI} = 0,$$

the bonds of the radical being equal to the number of atoms of hydrogen with which it is capable of combining.

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* Otis Coe Johnson, Negative Bonds and Rules for Balancing Equations. *Chemical News*, 1880, Vol. XLII. p. 51. Also, A Study of Oxidation and Reduction. Appendix to Douglas & Prescott: Qualitative Chemical Analysis. Third Revised Edition, 1881.

6. Metals in combination are usually positive. The most prominent exceptions are their compounds with hydrogen: $Sb^{-III}H_3{}^{+III}$.

Furthermore, as the oxidation of one substance must involve the reduction of some other, the number of bonds gained by the one, is lost by the other.

From these principles a rule is derived for writing equations of oxidation, if the products formed, are known. The rule is: "The number of bonds changed in one molecule of each, shows how many molecules of the other must be taken," the words *each* and *other* referring respectively to the oxidizing and the reducing agent.

Applying this method to the problem before considered:

$$K_2Mn_2O_8 + FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O.$$

Mn_2 in the first member has 14 bonds.
Mn_2 in the second member has 4 bonds.
Loss = 10.

Therefore the factor of $FeSO_4$ is 10.

Fe in the first member has 2 bonds.
Fe in the second member has 3 bonds.
Gain = 1,

and the factor of $K_2Mn_2O_8$ therefore is 1.

The amount of H_2SO_4 needed, must be determined according to the prescribed condition of the solution.

The Algebraic Method.—Methods resting on algebraical principles have also been devised for the constructing of chemical equations.*

To illustrate these, the former problem is here solved once more:

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* J. Bottomley, *Chemical News*, 1878, Vol. XXXVII. p. 110. Schwanert, Lehrbuch der Pharmaceutischen Chemie.

$$
\begin{aligned}
&a\mathrm{K_2Mn_2O_8} + b\mathrm{FeSO_4} + c\mathrm{H_2SO_4} \\
&\qquad = x\mathrm{K_2SO_4} + y\mathrm{MnSO_4} + z\mathrm{Fe_2(SO_4)_3} + w\mathrm{H_2O}.
\end{aligned}
$$

$$
\begin{array}{ll}
(1) & a = x; \\
(2) & 2a = y; \\
(3) & 8a + 4b + 4c = 4x + 4y + 12z + w; \\
(4) & b = 2z; \\
(5) & b + c = x + y + 3z; \\
(6) & 2c = 2w.
\end{array}
$$

Substituting in (3),

$$8a + 4b + 4c = 4a + 8a + 6b + c; \text{ or,}$$

$$(7) \quad 3c = 4a + 2b.$$

And also:

$$
\begin{array}{lll}
\text{From (4)} & & b = 2z, \quad \text{and} \\
\text{“} & (5) & b + c = x + y + 3z \\
\hline
 & & c = x + y + z, \quad \text{and} \\
\text{“} & \text{(1) and (2)} & \\
 & & c = a + 2a + \tfrac{1}{2}b.
\end{array}
$$

Multiplying by 4,

$$(8) \quad 4c = 12a + 2b.$$

Combining (7) and (8):

$$
\begin{array}{lrcl}
 & (7) \; 3c & = & 4a + 2b \\
 & (8) \; 4c & = & 12a + 2b \\
\hline
 & c & = & 8a \\
\hline
\text{From} & (7) \; 6c & = & 8a + 4b \\
\text{“} & (8) \; 6c & = & 18a + 3b \\
\hline
 & 0 & = & -\,10a + b
\end{array}
$$

Whence:

$$
\begin{aligned}
x &= a; \\
y &= 2a; \\
z &= 5a; \\
w &= 8a; \\
b &= 10a; \\
c &= 8a;
\end{aligned}
$$

and therefore:

$$
\begin{aligned}
&\mathrm{K_2Mn_2O_8} + 10\mathrm{FeSO_4} + 8\mathrm{H_2SO_4} \\
&\qquad = \mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 5\mathrm{Fe_2(SO_4)_3} + 8\mathrm{H_2O}.
\end{aligned}
$$

As will be seen, in this method the whole matter resolves itself into the solving of a set of simultaneous equations.

Calculation of Chemical Problems.

In studying chemical reactions, a variety of problems present themselves for consideration.

Many of these offer no difficulty whatever, and perhaps can be most conveniently solved by expressing the reaction in the form of an equation and then making a proportion:

As the symbol (formula) of the substance given, is to the symbol (formula) of the substance required, so is the weight of the substance given, to the weight of the substance required. The antecedents of the proportion must of course represent similar terms.

Substitute the numerical values for the symbols (formulæ), and solve the proportion in the usual manner.

Calculation of the Molecular Mass of a Substance.—

A. Given:

The formula;

The atomic masses.

Example: Calculate the molecular mass of $CaCO_3$.

	Number of Atoms in the Molecule.		Atomic Mass.		
Ca	1	×	40	=	40
C	1	×	12	=	12
O	3	×	16	=	48
			Molecular mass	=	100

B. Given:

The weight of one constituent in a given weight of a compound;

The total atomic mass of that constituent in the compound.

Example: Calculate the molecular mass of ethylic iodide from the following data:

7.5 grammes of this substance contain 6.106 grammes of iodine. The total atomic mass of iodine in one molecule is 127.

$$\begin{gathered} I : x :: 6.106 : 7.5 \\ 127 : x :: 6.106 : 7.5 \\ x = 156. \end{gathered}$$

That is, the molecular mass of ethylic iodide is 156.

Calculation of the Amount of any Constituent in a Compound.—

Example : How much S is contained in 1.230 grammes of FeS ?

$$\begin{gathered} FeS : S :: 1.23 : x \\ 88 : 32 :: 1.23 : x \\ x = 0.4475. \end{gathered}$$

That is, in 1.23 grammes of FeS there are 0.4475 gramme of S.

The calculation of the amount of any group or radical in a compound, is of course effected in a similar manner.

Example : How much CO_2 is contained in 5.530 grammes $CaCO_3$?

$$\begin{gathered} CaCO_3 : CO_2 : : 5.530 : x \\ 100 : 44 : : 5.53 : x \\ x = 2.4332. \end{gathered}$$

That is, 5.530 grammes of $CaCO_3$ contain 2.4332 grammes of CO_2.

Calculation of the Amount of a Compound which can be produced from a Given Amount of any of its Constituents.—

Given:

The molecular mass of the compound;

The total atomic mass of the constituent in a molecule of the compound.

Example : How much H_2SO_4 can be made from 17.50 grammes of S ?

$$\begin{gathered} S : H_2SO_4 : : 17.50 : x \\ 32 : 98 : : 17.50 : x \\ x = 53.594. \end{gathered}$$

Hence, 53.594 grammes of H_2SO_4 can be made from 17.50 grammes of S.

Calculation of the Percentage Composition of a Compound from its Formula.—

EXAMPLE: Calculate the percentage composition of ethyl alcohol from its formula C_2H_6O.

	Number of Atoms in the Molecule.		Atomic Mass.		
C	2	×	12	=	24
H	6	×	1	=	6
O	1	×	16	=	16
			Molecular mass	=	46

Then, making the proportion:
Molecular mass : Total atomic mass : : 100% : x % of each constituent, and applying this formula in turn to all constituents:

		Per cent.
C	$46 : 24 : : 100 : x$	$x = 52.18$
H	$46 : 6 : : 100 : x$	$x = 13.04$
O	$46 : 16 : : 100 : x$	$x = 34.78$

Calculation of the Chemical Formula of a Compound from its Percentage Composition.—

a. Calculation of the empirical formula.

b. Calculation of the molecular formula.

These methods of calculation have been fully explained in a previous chapter, to which reference should be made.

But, in considering problems of this type, there is one form, which calls for special consideration. It relates to the,

c. Calculation of the formulæ of minerals.

In mineralogy, formulæ like:

$$R''CO_3,$$
$$RO.CO_2,$$
$$R''.SiO_3,$$
$$RO.SiO_2,$$

are frequently employed.

These formulæ mean, that basic radicals of the same class may replace each other to an undetermined extent, and yet represent a type of mineral identical in respect to crystalline form, and other physical properties. Groups of minerals answering this description, are called isomorphous groups. Their formulæ are determined by the so-called oxygen ratio, which is found by calculating the percentages of oxygen present in the bases of the same type, considering the bases as anhydrous oxides, and the percentage of oxygen in the acid anhydrides, and comparing these values.

In Dana's Mineralogy, for instance, the two following analyses are quoted for siderite, which, theoretically is $FeCO_3$:

Constituents.	A.	B.
CO_2	= 38.35 per cent.	38.85 per cent.
FeO	= 55.64 "	47.20 "
MnO	= 2.80 "	8.34 "
MgO	= 1.77 "	3.78 "
CaO	= 0.92 "	0.63 "

Calculating the percentages of oxygen:

	A.	B.
O in CO_2..........	= 27.890	28.254
" " FeO..........	= 12.340	10.489
" " MnO	= 0.631	1.879
" " MgO	= 0.708	1.512
" " CaO..........	= 0.263	0.180

The sum of the oxygen in the basic anhydrides is respectively:

For A, 13.942;
" B, 14.060.

Comparing the percentages of oxygen in the CO_2 with that in the basic anhydrides, the ratio in both cases is essentially as 2 : 1.

Hence the type formula of this mineral is written as $RO.CO_2$ or as $R''CO_3$.

Formulæ of a similar kind are constantly used to indicate the composition of silicates.

These silicates may consist of metals of any valence, i.e., of monads, dyads, tetrads, etc., in combination with silica, SiO_2.

In these instances a concise formula could probably not be obtained if the ordinary methods of calculation were used, but, on replacing the weight of any constituent by an equivalent weight of some other substance isomorphous with it, a simpler relation among the constituents is readily established.

The following will illustrate:

A Swedish garnet yielded on analysis:

$$\begin{aligned} SiO_2 &= 36.62 \\ Al_2O_3 &= 7.53 \\ Fe_2O_3 &= 22.18 \\ CaO &= 31.80 \\ MgO &= 1.95 \\ \hline & \ 100.08 \end{aligned}$$

Among the constituents of this mineral, the iron and the aluminium, on the one hand, and the calcium and the magnesium, on the other, are possessed of respectively the same valence.

The iron sesquioxide can therefore be replaced by an equivalent amount of aluminium sesquioxide, or *vice versa*, and, in the same manner, an equivalent amount of calcium oxide can be made to replace the magnesium oxide determined by analysis, or *vice versa*. Thus:

$$Fe_2O_3 : Al_2O_3 :: 22.18 : x$$

$$160 : 102 :: 22.18 : x$$

$$x = 14.14.$$

$$MgO : CaO :: 1.95 : x$$

$$x = 2.73\ CaO.$$

These numbers express that 14.14 + 7.53 parts of Al_2O_3, i.e., a total of 21.67 parts of Al_2O_3, are equivalent to a mixture of 7.53 parts of Al_2O_3 and 22.18 parts of Fe_2O_3, and that 2.73 + 31.80 parts of CaO, i.e., a total of 34.53 parts of CaO, are equivalent to 31.80 parts of CaO and 1.95 of MgO.

The numbers thus obtained are:

$$\begin{aligned} SiO_2 &= 36.62, \\ Al_2O_3 &= 21.67, \\ CaO &= 34.53. \end{aligned}$$

Proceeding now as in any other instance of the calculation of a formula from percentage composition, a simple ratio is obtained between the constituents.

$$\begin{aligned} SiO_2 &= 36.62 \div 60 = .60 = 3, \\ Al_2O_3 &= 21.67 \div 102 = .20 = 1, \\ CaO &= 34.53 \div 56 = .60 = 3. \end{aligned}$$

The result of course will be the same if the percentages are divided by the molecular masses, and the amounts of the oxides which are isomorphous, are then added together. Thus:

$$\begin{aligned} SiO_2 &= 36.62 \div 60 = 0.6103, \\ Al_2O_3 &= 7.53 \div 102 = 0.0738, \\ Fe_2O_3 &= 22.18 \div 160 = 0.1380, \\ CaO &= 31.80 \div 56 = 0.5678, \\ MgO &= 1.95 \div 40 = 0.0487. \end{aligned}$$

Adding respectively the values for Al_2O_3 and for Fe_2O_3, and the values for CaO and for MgO, there results:

$$\begin{aligned} SiO_2 &= 0.6103 = 3, \\ (Al_2O_3.Fe_2O_3) &= 0.2118 = 1, \\ (CaO.MgO) &= 0.6165 = 3; \end{aligned}$$

which result is the same as that previously obtained. The formula of the mineral as derived from these data can be expressed as:

$$3(CaMgO),(Al_2Fe_2O_3),3SiO_2,$$

or as:

$$(CaMg)_3(Al_2Fe_2)Si_3O_{12}.$$

In accordance with the custom of mineralogists, who prefer to represent the formulæ of such minerals even more concisely, the letter R can be used to denote metallic radicals, and Roman numerals placed above the same, can be made to indicate the valence of the radicals:

The above formula would thus be written:

$$\overset{II}{R}_3(\overset{VI}{R_2})\overset{IV}{Si}_3O_{12},$$

a shorter, and an equally correct expression of the composition of this mineral.

A formula of this kind can easily be changed to a formula in the old dualistic system, by converting $\overset{II}{R}$ into RO and $(\overset{VI}{R_2})$ into R_2O_3. It would then read:

$$3RO,R_2O_3,Si_3O_6.$$

Comparing now the quantities of oxygen in combination with the several bases and with the silicon, it will be seen that they bear to one another the relation 3 : 3 : 6; that is, as 1 : 1 : 2. This ratio, in this instance 1 : 1 : 2, is termed the oxygen ratio, and it will be noticed that it is the same as the ratio of the total valence, the so-called atomic ratio, of each radical in the formula:

$$\overset{II}{R}_3(\overset{VI}{R_2})\overset{IV}{Si}_3.$$

For,

$$\begin{aligned} \text{II} \times 3 &= 6; \\ \text{VI} \times 1 &= 6; \\ \text{IV} \times 3 &= 12. \end{aligned}$$

and 6 : 6 : 12, is the same ratio as 1 : 1 : 2.

If it be required to calculate the mineralogical formula of a silicate from its percentage composition, the first step to be taken will be the calculation of the atomic ratio.

This is readily effected by observance of the following rule:

Divide the percentage composition of each constituent by its atomic mass, multiply by its valence, and deduce the ratio from the resulting numbers.

EXAMPLE.—The percentage composition of pyroxene is given as:

FeO = 8.00 per cent.
CaO = 24.90 " "
MgO = 13.40 " "
SiO_2 = 53.70 " "

Calculate the mineralogical formula.

Proceeding as directed,

$$\begin{array}{lrl} FeO & 8.0 \div 72 = 0.111 \times \text{II} & = 0.222 \\ CaO & 24.9 \div 56 = 0.446 \times \text{II} & = 0.892 \\ MgO & 13.4 \div 40 = 0.335 \times \text{II} & = \underline{0.670} \\ & & 1.784 \\ SiO_2 & 53.7 \div 60 = 0.895 \times \text{IV} & = 3.580 \end{array}$$

and the ratio is therefore,

1.784 : 3.580

that is, as 1 : 2.

Having thus obtained the atomic ratio, multiply this ratio by some number which will make the products divisible by the valence of the several classes of radicals, and then divide by the valence of the respective radicals.

The atomic ratio in this problem was found to be:

$$\overset{\text{II}}{R},\ \overset{\text{IV}}{Si_2}.$$

Multiplying through by 2, and dividing by the valences II and IV respectively, there is obtained :

$$\frac{1 \times 2}{\text{II}} : \frac{2 \times 2}{\text{IV}}$$

$$\frac{2}{\text{II}} : \frac{4}{\text{IV}}$$

$$1 : 1$$

and the mineralogical formula of pyroxene is therefore:

$$\text{RO}, \quad \text{SiO}_2.$$

Methods of Indirect Analysis.

The quantitative determination of certain constituents in substances, is sometimes effected by methods of indirect analysis.

As an illustration of these methods, the following types will be considered: The residue method, the substitution method, and the method which is based on numerical differences between molecular masses.

I. The Residue Method.—The substance is chemically acted upon by a reagent which is added in known quantity, but in excess. This excess is determined, and the amount of the substance sought is calculated from the data thus obtained.

EXAMPLE.—Calculate the amount of CO_2 in a sample of impure $CaCO_3$ from the following data: 0.305 gramme $CaCO_3$ were dissolved in 35 c. c. of normal HNO_3. The HNO_3 which remained uncombined was neutralized by a solution of normal NaOH, of which 30.0 c. c. were used.

Total HNO_3............................= 35.0 c. c.
HNO_3 neutralized by NaOH..............= 30.0 c. c.

HNO_3 neutralized by $CaCO_3$..............= 5.0 c. c.
1 c. c. normal HNO_3......................= 0.063 HNO_3.
5 c. c. " " ....= 0.315 HNO_3.

$$2\,HNO_3 + CaCO_3 = Ca(NO_3)_2 + CO_2 + H_2O.$$

$$2HNO_3 : CO_2 :: 0.315 : x$$

$$126 : 44 :: 0\ 315 : x$$

$$x = 0.110 \text{ gramme } CO_2.$$

$$0.305 : 0.110 :: 100 : x$$

$$x = 36.06\%\ CO_2.$$

II. The Substitution Method.—The substance to be determined is replaced by an equivalent amount of some other substance, which is directly determined, and from this the value sought is then calculated.

EXAMPLE.—Determine the strength of a solution of chlorine from the following data:

A solution of potassium iodide was added in excess to 100 c. c. of the chlorine solution. A standard solution of $Na_2S_2O_3$ was used to determine the iodine which was set free, and 50 c. c. of the $Na_2S_2O_3$ (sodium thiosulphate) solution were used.

1 c. c. $Na_2S_2O_3$ solution.................... = 0.01268 I.
50 c. c. $Na_2S_2O_3$ " .... = 0.63400 I.

Hence 0.6340 gramme iodine was liberated.

Atomic mass of I................ .... = 126.8
" " " Cl... .... = 35.5

$$KI + Cl = KCl + I$$

$$I : Cl :: 0.6340 : x$$

$$126.8 : 35.5 :: 0.6340 : x$$

$$x = 0.1775.$$

Hence 0.1775 gramme of chlorine is contained in 100 c. c. of the chlorine solution, and 1 c. c. of the solution contains 0.001775 gramme of chlorine.

III. The Method based on Numerical Differences between Molecular Masses.—Two divisions of this method must be recognized:

A. The components of the mixture have one constituent in common.

B. The components of the mixture have more than one constituent in common.

A. In a mixture of two salts which have one constituent in common and which differ in their molecular masses, the common constituent and the combined weight of the two salts are determined, and from these data the amounts of the other constituents are calculated.

Example 1.—*Mixed Silver Salts.*—Given, the weight of a precipitate, consisting of the mixed chloride and bromide of silver, and the weight of the silver therein contained. Required, to calculate the proportions of chlorine and bromine in the sample.

If the common constituent be calculated to its combination with the element or group having the lowest atomic or molecular mass, the figure obtained will fall short of the given amount of the mixed salts, by an amount proportional to the excess of the higher combining mass over the lesser.

$AgBr + AgCl = 0.75$; Cl atomic mass $= 35.5$;
Ag therefrom $= 0.50$; Br " " $= 80$.

Calculating all the Ag to its equivalent of AgCl:

$$\begin{aligned} Ag : AgCl &:: 0.50 : x \\ 108 : 143.5 &:: 0.50 : x \\ 71.75 &= 108x \\ 0.6643 &= x. \end{aligned}$$

Then, 0.7500
less 0.6643

0.0857 excess due to Br.

$$\begin{aligned} Br - Cl : Br &:: .0857 : x \\ 44.5 : 80 &:: .0857 : x \\ 6.8560 &= 44.5x \\ 0.1540 &= x. \end{aligned}$$

Hence, the $Br = 0.1540$.

0.7500 is the total amount of the mixed silver salts.

$Ag = 0.5000$
$Br = 0.1540$
$Ag + Br = 0.6540$

0.7500
less 0.6540

$Cl = 0.0960$

Hence, Ag present $= 0.5000$
Br " $= 0.1540$
Cl " $= 0.0960$

The results may be thus verified :

$$
\begin{aligned}
\mathrm{Br} : \mathrm{AgBr} &:: 0.154 : x \\
80 : 188 &:: 0.154 : x \\
28.952 &= 80x \\
0.3619 &= x. \\
\therefore\ \mathrm{AgBr} &= 0.3619.
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{Cl} : \mathrm{AgCl} &:: .096 : x \\
35.5 : 143.5 &:: .096 : x \\
13.776 &= 35.5x \\
0.3881 &= x. \\
\therefore\ \mathrm{AgCl} &= 0.3881.
\end{aligned}
$$

$$
\begin{aligned}
\text{Hence,}\qquad \mathrm{AgBr} &= 0.3619 \\
\mathrm{AgCl} &= \underline{0.3881} \\
\text{Total } \mathrm{AgCl} + \mathrm{AgBr} &= 0.7500
\end{aligned}
$$

EXAMPLE 2.—*Mixed Sulphates.*—Given, the weight of a precipitate consisting of the mixed sulphates of potassium and sodium, 0.371 gramme. SO_3 present therein, 0.200 gramme. Required, the amount of Na_2O and the amount of K_2O in the sample.

Calculating all the SO_3 to its equivalent of Na_2SO_4 :

$$
\begin{aligned}
\mathrm{SO_3} : \mathrm{Na_2SO_4} &:: 0.200 : x \\
80 : 142 &:: 0.2 : x \\
28.4 &= 80x \\
0.355 &= x.
\end{aligned}
$$

that is, all of the SO_3 present would be equivalent to 0.355 Na_2SO_4.

Subtracting this from the total of the mixed sulphates:

$$0.371 - 0.355 = 0.016,$$

which amount is due to the higher atomic mass of the potassium. Hence,

$$
\begin{aligned}
\mathrm{K_2O} - \mathrm{Na_2O} : \mathrm{K_2O} &:: .016 : x \\
32 : 94 &:: .016 : x \\
1.504 &= 32x \\
0.047 &= x.
\end{aligned}
$$

Hence, the KO_2 present is equal to 0.047, and:

$$0.371 - \left[\begin{array}{cc} K_2O + & SO_3 \\ 0.047 & 0.200 \end{array}\right] = Na_2O \text{ present};$$

$$\begin{array}{rl} & 0.371 \\ & 0.247 \\ \cline{2-2} Na_2O \text{ present} = & 0.124 \end{array}$$

To check the results obtained:

$$\begin{aligned} K_2O : K_2SO_4 &: : 0.047 : x \\ 94 : 174 &: : 0.047 : x \\ 8.178 &= 94x \\ 0.087 &= x. \end{aligned}$$

That is, $K_2SO_4 = 0.087$.

$$\begin{aligned} Na_2O : Na_2SO_4 &: : 0.124 : x \\ 62 : 142 &: : 0.124 : x \\ 17.608 &= 62x \\ 0.284 &= x. \end{aligned}$$

That is, $Na_2SO_4 = 0.284$.

$$\begin{array}{rl} K_2SO_4 = & 0.087 \\ Na_2SO_4 = & 0.284 \\ \cline{2-2} \text{Total mixed sulphates} = & 0.371 \end{array}$$

B. In a mixture of two salts which have more than one constituent in common, the amounts of these common constituents are determined and then calculated to their respective combinations.

This class of problems can be readily solved by arithmetic, but perhaps even more conveniently by algebraic methods, as the following will show:

EXAMPLE.—In a sample of commercial bicarbonate of soda there are present:

Sodium oxide = 32.00 per cent.
Carbon dioxide = 45.00 "

Calculate the amount of sodium monocarbonate and of sodium bicarbonate in the sample.

Sodium monocarbonate $Na_2CO_3 = Na_2O + CO_2$.
Sodium bicarbonate $2NaHCO_3 = Na_2O + 2CO_2 + H_2O$.

The first step to be taken is to calculate all the Na_2O to its equivalent in CO_2:

$$Na_2O : CO_2 :: 32.0 : x$$
$$62 : 44 :: 32.0 : x$$
$$x = 22.7096 CO_2.$$

This amount of CO_2 would be required to transform all of the Na_2O into Na_2CO_3 (monocarbonate), but as the main portion of the sodium oxide is present in the form of $NaHCO_3$ (bicarbonate), there is needed this amount of CO_2, 22.7096 per cent, and as much more as is necessary to form the bicarbonate.

As $2NaHCO_3 = Na_2O + 2CO_2 + H_2O$, the difference between the total CO_2 in the sample, and the above amount, 22.7096 per cent, must be multiplied by 2, and this product calculated to sodium bicarbonate. Thus:

Total CO_2 in sample, 45.0000 per cent,
less 22.7096 "
22.2904 per cent.

$$22.2904 \times 2 = 44.5808$$
$$CO_2 : NaHCO_3 :: 44.6 : x$$
$$44 : 84 :: 44.5808 : x$$
$$x = 85.108 \text{ per cent.}$$

Hence, $NaHCO_3 = 85.1100$

Total $CO_2 = 45.0000$
CO_2 combined in the form of bicarbonate $= 44.5808$
$CO_2 = 0.4192$

which must be calculated as present in the form of monocarbonate.

$$CO_2 : Na_2CO_3 :: 0.4192 : x$$
$$44 : 106 :: 0.4192 : x$$
$$x = 1.01.$$

Hence, $Na_2CO_3 = 1.01$ per cent,

and the sample therefore contains:

$NaHCO_3 = 85.11$ per cent,
$Na_2CO_3 = 1.01$ "

To prove the correctness of the results thus obtained, a check calculation is easily made. Thus:

$$Na_2CO_3 : CO_2 :: 1.01 : x$$
$$106 : 44 :: 1.01 : x$$
$$x = 0.41.$$
$$NaHCO_3 : CO_2 :: 85.11 : x$$
$$84 : 44 :: 85.11 : x$$
$$x = 44.59;$$

that is,

CO_2 in form of $Na_2CO_3 = 0.41$
CO_2 " " $NaHCO_3 = 44.59$
Total $= 45.00$

which corresponds to the amount as found by analysis.

The same problem can be solved by algebra in the following manner:

$CO_2 = 45.00$ per cent,
$Na_2O = 32.00$ "

Let x = percentage of Na_2CO_3;
y = " " $NaHCO_3$.

Then,

$$\frac{CO_2}{Na_2CO_3}x + \frac{CO_2}{NaHCO_3}y = 45$$

$$\frac{Na_2O}{Na_2CO_3}x + \frac{Na_2O}{2NaHCO_3}y = 32.$$

Substitute the molecular masses in their proper places, and solve for y.

$$y = 85.11$$

Hence, $NaHCO_3 = 85.11$ per cent.

$85.11 : x :: 2NaHCO_3 : Na_2O$

$85.11 : x :: 168 : 62$

$x = 31.41$ per cent Na_2O present as $NaHCO_3$.

Total Na_2O in sample $= 32.00$

Na_2O present as $NaHCO_3 = 31.41$

Na_2O " " $Na_2CO_3 = 0.59$

$Na_2O : Na_2CO_3 :: 0.59 : x$

$62 : 106 :: 0.59 : x$

$x = 1.01$ per cent.

Hence, the sample contains:

$NaHCO_3 = 85.11$ per cent

$a_2CO_3 = 1.01$ "

CHAPTER VIII.

VOLUME AND WEIGHT RELATIONS OF GASES.

Volume Relations of Gases.—The ratio of weights of equal volumes of elements, in the form of gas, is the same as the ratio of their atomic masses. Exceptions to this are the elements zinc, mercury, cadmium, phosphorus, and arsenic, which will be considered later. Thus:

One litre of:	*weighs:*	*Atomic Mass.*
Hydrogen	0.0896 gramme	1
Oxygen	1.4295 grammes	16
Nitrogen	1.2555 "	14

From these figures it appears that, weighing equal volumes, oxygen weighs about sixteen times as much, and nitrogen about fourteen times as much, as hydrogen.

Strictly speaking, 1.4295 is only 15.9 times 0.0896, and 1.2555 is a trifle over 14 times 0.0896, but the unavoidable errors of experiment will account for these differences.

One litre of hydrogen weighs 0.0896 gramme. This value is termed a crith, and therefore one litre of hydrogen is said to weigh one crith. As oxygen weighs sixteen times as much as hydrogen, one litre of oxygen is said to weigh 16 criths, one litre of nitrogen weighs 14 criths, and so on.

The following table, prepared by the writer, may prove convenient for reference in calculations concerning gases.

1	2	3	4	5	6	7	8
NAME.	Symbol.	½ Mol. Wt.	$H_2 = 1.0$	Air = 1.0	OBSERVERS.	Weight in grammes of 1000 c.c. at 0° C. and 760 mm.	Weight in grains of 100 cubic inches at 60° F. and 30 inches.
Hydrogen	H_2	1.00	1.00	0.0693	**Regnault.**	0.0896	2.1437
Air			14.43	1.0000		1.293	30.935
Alcohol	C_2H_5OH	23.00	23.275	1.613	**Gay-Lussac.**	2.0856	49.8981
Ammonia	NH_3	8.50	8.528	0.591	**Davy. Thomson.**	0.7641	18.2825
Aqueous Vapor	H_2O	9.00	8.997	0.6235	**Gay-Lussac.**	0.8061	19.2879
Arsenic	As_4	149.8	147.186	10.2	**Deville. Troost.**	13.1886	315.5370
Arseniuretted Hydrogen	AsH_3	38.95	38.888	2.695	**Dumas.**	3.4846	83.3698
Bromine	Br_2	79.7	79.942	5.54	**Mitscherlich.**	7.1632	171.3799
Carbon Monoxide	CO	14.0	13.953	0.967	**Von Wrede.**	1.2503	29.9141
Carbon Dioxide	CO_2	22.0	22.063	1.529	**Regnault.**	1.9769	47.2996
Carbon Disulphide	CS_2	38.0	38.167	2.645	**Gay-Lussac.**	3.4199	81.8230
Chlorine	Cl_2	35.4	35.209	2.44	**V. & C. Meyer.**	3.1549	75.4814
Cyanogen	$(CN)_2$	26.0	26.060	1.806	**Gay-Lussac.**	2.3351	55.8686
Ether	$C_4H_{10}O$	37.0	37.315	2.586	**Gay-Lussac.**	3.3436	79.9979
Ethyl	$(C_2H_5)_2$	29.0	28.860	2.00	**Frankland.**	2.5860	61.8700
Ethylene	C_2H_4	14.0	14.112	0.978	**Saussure.**	1.2645	30.2544
Hydrobromic Acid	HBr	40.35	39.105	2.71	**Löwig.**	3.5040	83.8338
Hydrochloric Acid	HCl	18.2	18.326	1.27	**Biot. Gay-Lussac.**	1.6421	39.2874
Hydrocyanic Acid	HCN	13.5	13.665	0.947	**Gay-Lussac.**	1.2244	29.2954
Hydriodic Acid	HI	63.75	64.112	4.443	**Gay-Lussac.**	5.7447	137.4442
Iodine (below 700°)	I_2	126.5	125.771	8.716	**Dumas.**	11.2697	269.6294
Iodine (above 1400°)	I	63.25	66.378	4.6	**Crafts. Meier.**	5.9478	142.3010
Mercury	Hg	100.00	100.663	6.976	**Dumas.**	9 0199	215.8025
Mercuric Chloride	$HgCl_2$	135.40	141.414	9.8	**Mitscherlich.**	12.6714	303.1630
Mercurous Chloride	Hg_2Cl_2	235.40	118.470	8.21	**Deville. Troost.**	10.6155	253.9763
Methane	CH_4	8.00	8.046	0.5576	**Thomson.**	0.7209	17.2493

1 NAME.	2 Symbol.	3 ½ Mol. Wt.	4 $H_2 = 1.0$	5 Air = 1.0	6 OBSERVERS.	7 Weight in grammes of 1000 c. c. at 0° C. and 760 mm.	8 Weight in grains of 100 cubic inches at 60° F. and 30 inches.
Nitrogen	N_2	14.00	14.011	0.971	**Regnault.**	1.2555	30.0378
Nitric Oxide	NO	15.00	14.978	1.038	**Berard.**	1.3421	32.1105
Nitric Peroxide	NO_2	23.00	24.819	1.72	**Mitscherlich.**	2.2239	53.2082
Nitrous Oxide	N_2O	22.00	22.034	1.527	**Thomson.**	1.9744	47.2377
Oxygen	O_2	16.00	15.953	1.1056	**Regnault.**	1.4295	34.2017
Ozone	O_3	24.00	24.00	1.6632	*Calculated.*	2.1505	51.4510
Phosphorus	P_4	62.00	63.780	4 42	**Dumas.**	5.7150	136.7327
Phosphuretted Hydrogen	PH_3	17.60	17.085	1.184	**Dumas.**	1.5309	36.6270
Selenium	Se_2	79.00	81.962	5.68	**Deville. Troost.**	7.3442	175.7108
Seleniuretted Hydrogen	H_2Se	40.50	40.331	2 795	**Bineau.**	3.6139	86.4633
Sulphur (above 860°)	S_2	32.00	32.178	2.23	**Deville. Troost.**	2.8833	68.9850
Sulphur (at 450°)	S_6	96.00	95.483	6.617	**Dumas.**	8.5557	204 6968
Sulphuretted Hydrogen	H_2S	17.00	17.186	1.191	**Thénard. Gay-Lussac.**	1.5399	36.8435
Sulphuric Oxide	SO_3	40.00	39.870	2.763	**Marignac.**	3.5725	85.4734
Sulphurous Oxide	SO_2	32.00	32.236	2.234	**Thénard.**	2.8885	69.1087

The figures in column 5 are direct observations by the authorities named in column 6.

The figures in column 4 are all calculated from Regnault's determination of the Specific Gravity of Hydrogen 0 0693.

The figures in column 7 are calculated from Regnault's determination of the weight of 1000 c. c. of air, 1.293 grammes.

The figures in column 8 are calculated from Regnault's data as follows: (Miller: Elements of Chemistry, Vol. I. p. 183.)

1 litre of air at 32° F. and under a pressure of 29.922 inches of mercury weighs 1.293187 grammes.
1 litre = 61.024 cubic inches.
1 gramme = 15.433 grains.
Expansion of air between 32° F. and 60° F. by heat is such that 100.000 parts become 105.701.
Barometric pressure of 29.922 inches at 32° F. = 30.005 inches at 60° F.
These give the weight of 100 cubic inches of air = 30.935 grains.

The exceptions before referred to, when it was stated, that the ratio of weights of equal volumes of elements in the gaseous condition are the same as the ratio of their atomic masses, are zinc, cadmium, mercury, phosphorus, and arsenic.

One litre of:	*weighs:*	*Atomic Mass.*
Zinc as gas	2.9344 grammes	65.5
Mercury " "	9.0199 "	200
Cadmium " "	5.0944 "	112

$$\begin{aligned} 2.9344 \div 0.0896 &= 32.75 \\ 9.0199 \div 0.0896 &= 100.66 \\ 5.0944 \div 0.0896 &= 56.85 \end{aligned}$$

or, in the cases of Zinc,
Mercury,
Cadmium, } it is practically one half their atomic masses.

One litre of:	*weighs:*	*Atomic Mass.*
Phosphorus as gas	5.7150 grammes	31
Arsenic " "	13.1886 "	75

Therefore, in the case of these elements,

$$\begin{aligned} 5.7150 \div 0.0896 &= 63.78 \\ 13.1886 \div 0.0896 &= 147.19, \end{aligned}$$

it is practically equal to twice their atomic masses.

Excepting then, zinc, mercury, cadmium, phosphorus, and arsenic, it has been found that when the elements in gaseous form are made to combine, two volumes of gas always result; no matter what may be the number of volumes that enter into the compound, they invariably become condensed into two volumes. Thus:

1 vol. H and 1 vol. Cl form 2 vols. HCl;
2 vols. H " 1 " O " 2 " H_2O;
3 " H " 1 " N " 2 " NH_3.

Compound gases in forming chemical combinations, behave in the same manner. Thus:

$$2 \text{ volumes } CO + 1 \text{ volume } O_2 = 2 \text{ volumes } CO_2.$$

In the case of zinc, mercury, and cadmium,

$$\begin{array}{llllll} 2 \text{ vols. } & Zn + 2 & \text{vols. } Cl & = 2 & \text{vols. } & ZnCl_2; \\ 2 \text{ ``} & Hg + 2 & \text{``} \quad Cl & = 2 & \text{``} & HgCl_3; \\ 2 \text{ ``} & Cd + 2 & \text{``} \quad Cl & = 2 & \text{``} & CdCl_2. \end{array}$$

and in the case of phosphorus and arsenic,

$$\begin{array}{llllll} \frac{1}{2} \text{ vol. } & P + 3 & \text{vols. } H & = 2 & \text{vols. } & PH_2; \\ \frac{1}{2} \text{ ``} & As + 3 & \text{``} \quad H & = 2 & \text{``} & AsH_3. \end{array}$$

From these data there may be deduced the:

Law of Volumes—first advanced in 1805 by Gay-Lussac and Von Humboldt. This law reads:

The ratio in which gases combine by volume is always a simple one, and the volume of the resulting gaseous product bears a simple ratio to the volumes of its constituents.

A careful consideration of the data above recorded, warrants the following more precise formulation of the law:

The combining volumes of all elementary gases are equal, excepting those of zinc, mercury, and cadmium, which are twice those of the other elements, and of phosphorus and arsenic, which are one half.

This law of volumes, originally discovered through direct experimental research, has lately, by Clausius, been shown to be most readily deduced from the law of Avogadro (1811).

Avogadro's law holds that:

Equal volumes of all gases contain the same number of molecules.

This law has not only been proved true by mathematical reasoning, but its correctness is affirmed by every known chemical and physical phenomenon having any bearing on the case.

The number of molecules in equal volumes being the same, if the molecules were diminished in number, these volumes would, of course, be diminished proportionally.

Neglecting for the present the exceptions noted (Zn, Hg, Cd, P, As), a molecule of any element in the gaseous condition can be assumed to consist of at least two atoms.

To illustrate this: Consider a litre selected as the unit of volume; consider also that it is possible to count the number of molecules in any given space, and further assume, that a litre contains one million molecules.

From the law of volumes it is known, that one litre of hydrogen, assumed to contain one million molecules of hydrogen, will combine with one litre of chlorine, assumed to contain one million molecules of chlorine, to form two litres of hydrochloric acid gas, containing two million molecules of HCl.

As the resulting gas contains two million molecules, each molecule of which contains hydrogen, each one of the original one million molecules of hydrogen must have consisted of, at least, two equal particles.

The same reasoning applies to the chlorine gas, and this demonstration will hold good, whatever number of molecules may be assumed as existing in a given space.

Again: Two litres of hydrogen, assumed to contain two million molecules of hydrogen, will combine with one litre of oxygen, assumed to contain one million molecules, to form two litres of water vapor, assumed to contain two million molecules.

Hence, in order to form two million molecules of H_2O, each molecule containing oxygen, each of the one million molecules of oxygen taken, must have consisted of at least two particles—atoms.

In the same manner it might be shown that each molecule of nitrogen must also consist of at least two particles, and, barring the exceptions noted, this argument might be applied to the entire list of elements obtainable in the form of gas.

If equal volumes of two monad elements, which can combine chemically, are placed together under the proper conditions, chemical combination will ensue, and the resulting compound will, in volume, be equal to the sum of the volumes of its constituents. Thus:

$$1 \text{ volume } H_2 + 1 \text{ volume } Cl_2 = 2 \text{ volumes } HCl,$$

and, as equal volumes contain the same number of molecules, this statement can be thus formulated :

$$\underset{\text{(2 atoms)}}{1 \text{ molecule H}} + \underset{\text{(2 atoms)}}{1 \text{ molecule Cl}} = \underset{\substack{\text{(Each of 2 atoms.}\\ \text{Total = 4 atoms.)}}}{2 \text{ molecules HCl},}$$

No change in volume has taken place.

If combination is to be effected between a dyad element and a monad element, each atom of the former requires two atoms of the latter. As the molecules of each element consist of two atoms, and as each molecule of the resulting compound consists of three atoms, there results :

$$\underset{\substack{\text{(Total of 4}\\ \text{atoms.)}}}{2 \text{ molecules H}} + \underset{\substack{\text{(Total of 2}\\ \text{atoms.)}}}{1 \text{ molecule O}} = \underset{\substack{\text{(Each of 3 atoms.}\\ \text{Total = 6 atoms.)}}}{2 \text{ molecules } H_2O.}$$

That is to say, three molecules have become condensed into two molecules, and as equal volumes contain the same number of molecules, this fact can be thus stated :

$$2 \text{ vols. } H_2 + 1 \text{ vol. } O_2 = 2 \text{ vols. } H_2O.$$

In an analogous manner, these relations can be reasoned out for triads, tetrads, etc., and also for the exceptions previously noted.

From what has been previously stated, it follows that to write correctly the symbol of an element when in the gaseous condition, its usual symbol must be doubled. Thus, when bromine is to be represented as a gas, its symbol should be written Br_2 and not Br; iodine as a gas should be expressed as I_2; and so on.

Zinc, mercury, cadmium, phosphorus, and arsenic of course are exceptions. As the molecules of the first three are monatomic, their symbols, even when the elements are to be represented as gases, are respectively Zn, Hg, and Cd.

Phosphorus and arsenic, on the other hand, when in the gaseous condition, are expressed by P_4 and As_4, respectively, because their molecules are tetra-atomic.

All of these considerations lead to the conclusion that :

The specific gravity of most elements in the gaseous condition is equal to their atomic mass,* and the specific gravity of compound gases is equal to one half their molecular mass.

The simple relations by volume, obtaining in cases of combination and decomposition of gaseous bodies, are perhaps best illustrated by a few examples.

EXAMPLES.

(*a*) What volume of hydrogen is required to combine with 20 c. c. of nitrogen to form ammonia gas (NH_3)?

The formula of NH_3 shows that:

$$1 \text{ vol. } N_2 + 3 \text{ vols. } H_2 = 2 \text{ vols. } NH_3.$$

In this case, the volume of the nitrogen is given as 20 c. c. Substituting the proper numerical equivalents in the above equation, there results:

$$20 \text{ c. c. } N_2 + 60 \text{ c. c. } H_2 = 40 \text{ c. c. } NH_3.$$

---

* *Exceptions.*—The specific gravity of zinc, mercury, and cadmium, when in the gaseous condition is equal to one half their atomic mass; the specific gravity of arsenic and phosphorus, when in the gaseous condition, is equal to twice their atomic mass.

(*b*) What volume of mercury gas will combine with 182 c. c. of chlorine gas to form mercuric chloride?

$$2 \text{ vols. } Hg + 2 \text{ vols. } Cl_2 = 2 \text{ vols. } HgCl_2.$$

The volume of the chlorine is given as 182 c. c. Hence,

$$182 \text{ c. c. } Hg + 182 \text{ c. c. } Cl_2 = 182 \text{ c. c. } HgCl_2.$$

(*c*) How much oxygen is required to burn 219 cubic feet of hydrogen gas?

$$2 \text{ vols. } H_2 + 1 \text{ vol. } O_2 = 2 \text{ vols. } H_2O.$$

The volume of the hydrogen is given as 219 cubic feet. Hence,

$$219 \text{ c. f. } H_2 + 109.5 \text{ c. f. } O_2 = 219 \text{ c. f. } H_2O.$$

(*d*) 22 litres of nitrogen trichloride were dissociated into the component gases. What was the volume of the mixed gases after dissociation?

$$2 \text{ vols. } NCl_3 = 1 \text{ vol. } N_2 + 3 \text{ vols. } Cl_2.$$

The volume of the nitrogen trichloride is given as 22 litres. Hence,

$$22 \text{ ls. } NCl_3 = 11 \text{ ls. } N_2 + 33 \text{ ls. } Cl_2.$$

(*e*) 125 c. c. of nitrogen gas and 210 c. c. of hydrogen gas can form what volume of NH_3? Which gas is in excess, and to what extent?

$$1 \text{ vol. } N_2 + 3 \text{ vols. } H_2 = 2 \text{ vols. } NH_3.$$

But the amount of nitrogen given is evidently more than sufficient to combine with the amount of hydrogen given. Therefore, as 210 c. c. = 3 vols., 1 vol. = 70 c. c., and therefore:

140 c. c. of NH_3 will be formed, and $125 - 70 = 55$ c. c. of N_2 will remain uncombined.

(*f*) Given 630 c. c. arsenic gas and 840 c. c. chlorine gas. How much $AsCl_3$ can be formed; which gas, and how much of it, remains uncombined?

$$\tfrac{1}{2} \text{ vol. } As_4 + 3 \text{ vols. } Cl_2 = 2 \text{ vols. } AsCl_3.$$

The arsenic gas is evidently in excess, for 630 is more than $\frac{1}{6}$ of the amount of chlorine given.

The amount of chlorine must therefore be made the basis of calculation.

$$3 \text{ vols.} = 840 \text{ c. c.}$$
$$\tfrac{1}{2} \text{ vol.} = 140 \text{ c. c.}$$

Hence, substituting the proper numerical values in above equation:

$$140 \text{ c. c. } As_4 + 840 \text{ c. c. } Cl_2 = 560 \text{ c. c. } AsCl_3.$$

This is the amount of the $AsCl_3$ formed; the arsenic gas is in excess, to the extent of 630 − 140 = 490 c. c.

Relation between Mass and Volume in Gases.

Chemical equations, besides representing the relations by weight of the various factors concerned, exhibit also, as has been previously stated, the volume relations obtaining between the different factors, when these are in the gaseous state.

Thus the equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O,$$

not only illustrates the fact that one molecule of methane combines with two molecules of oxygen to form one molecule of carbon dioxide and two molecules of water, but it shows also, that one volume of methane and two volumes of oxygen combine to form one volume of carbon dioxide and two volumes of water vapor.

The volume of any gas may be calculated from its weight, by dividing the latter by the weight of one litre of the gas or vapor; the quotient represents the volume in litres.

The weight in grammes of one litre of any element in the state of gas or vapor, under standard conditions, is found by the formula:

$$\text{Weight} = 0.0896 \times \text{atomic mass of the element.*}$$

---

* Of course in the case of zinc, mercury, and cadmium the formula reads, Weight $= 0.0896 \times \frac{1}{2}$ atomic mass; and in the case of phosphorus and arsenic, Weight $= 0.0896 \times 2$ atomic mass.

In the case of compound gases, the formula:

$$\text{Weight} = 0.0896 \times \tfrac{1}{2} \text{ molecular mass},$$

yields the desired result.

An example will illustrate the solving of problems of this kind.

EXAMPLE.—Given, 2.5 grammes of hydrogen and 7.5 grammes of chlorine to form hydrochloric acid gas. What is the weight, and what is the volume of the product? Which gas is in excess, and to what extent?

$$\text{Cl} : \text{H} :: 7.5 : x$$
$$35.5 : 1 :: 7.5 : x$$
$$x = 0.2111.$$

This shows that 0.2111 gramme of hydrogen is required to combine with 7.5 grammes of chlorine.

Total hydrogen..... = 2.5000 grammes.
Hydrogen required... = 0.2111 "
Hydrogen in excess.. = 2.2889 "

The weight of the HCl formed is:

7 5000 grammes.
0.2111 "
7.7111 "

The volume of the HCl is readily figured.

The weight of one litre of HCl is equal to:

$$0.0896 \times \tfrac{1}{2} \text{ mol. mass of HCl},$$
$$0.0896 \times \frac{36.5}{2} = 1.6352 \text{ grammes.}$$

The weight of the HCl produced is 7.7111 grammes, and this corresponds to:

$$7.7111 \div 1.6352 = 4.715 \text{ litres.}$$

The weight of the excess of hydrogen is 2.2889 grammes, and this corresponds to:

$$2.2889 \div 0.0896 = 25.5245 \text{ litres.}$$

The sum of the atomic masses indicated by a chemical symbol or formula is proportional to the mass (weight) of the substances involved in a chemical reaction, be these masses (weights) given in criths, or in any other unit. To express this in a formula, let:

$\left.\begin{matrix} m \\ m' \end{matrix}\right\}$ represent the molecular masses of any two substances.

$\left.\begin{matrix} n \\ n' \end{matrix}\right\}$ represent the number of their molecules in a given reaction.

Then nm and $n'm'$ represent the formulæ of these substances.

If W and W' express weight in criths, then:

$$nm : n'm' :: W : W'.$$

It will be remembered that the molecular mass of a body is equal to twice its specific gravity in the gaseous state, the specific gravity being referred to hydrogen as standard.

Therefore, if molecular mass is represented by m',

$$m' = 2 \text{ sp. gr.}$$

The weight of a body is equal to the product of its volume by its specific gravity.

If: weight $= W'$,
volume $= v$,
specific gravity $=$ sp. gr.,

$$W' = v \times \text{sp. gr.}$$

If in the proportion:

$$nm : n'm' :: W : W'$$

there are substituted the values:

$$m' = 2 \text{ sp. gr.}$$

and

$$W = v \times \text{sp. gr.},$$

there is obtained the expression:

$$nm : n'\ 2\ \text{sp. gr.} :: W : v \times \text{sp. gr.}$$
$$nm : 2n' :: W : v$$
$$\tfrac{1}{2}\ nm : n' :: W : v.$$

This formula permits the calculation of the *volume* of a gas or vapor involved in a chemical reaction, when the *weight* of some factor or product is known, and conversely, permits calculation of the weight, when the volume is given.

This may be formulated by expressing the reaction in the form of an equation and then making the proportion:

As one half the symbol (formula) of the substance whose *weight* is given or sought, is to the number of molecules of the substance whose *volume* is given or sought, so is the weight in criths of the first-named substance, to the volume in litres of the last-named substance.

Numbers are then substituted for the respective symbols (formulæ), and the calculation made as indicated.

EXAMPLES.

(*a*) What amount of potassium chlorate is required to yield 1.75 litres of oxygen?

$$2\ KClO_3 = 2KCl + 3O_2.$$
$$\tfrac{1}{2}(2KClO_3) : 3 :: x : 1.75$$
$$122.6 : 3 :: x : 1.75$$
$$3x = 214.55$$
$$x = 71.517 \text{ criths}$$
$$71.517 \times 0.0896 = 6.401 \text{ grammes.}$$

(*b*) How many litres of nitrous oxide can be obtained from 250.0 grammes ammonium nitrate?

$$NH_4NO_3 = 2H_2O + N_2O.$$
$$\tfrac{1}{2}(NH_4NO_3) : 1 :: \frac{250.0}{0.0896} : x$$
$$40 : 1 :: 2790.18 : x$$
$$40x = 2790.18$$
$$x = 69.75 \text{ litres.}$$

Analysis of Gases.

Introductory.—Gas analysis is divided into ultimate and proximate analysis. In ultimate analysis the gaseous compound or mixture is burned, and the amounts of the elements present are calculated from the amount of H_2O, of CO_2, the amount of residual gas, and the change in volume produced by the combustion.

In proximate analysis the various constituents of a gaseous mixture are absorbed by certain reagents, successively applied.

The comparative amounts of the gases present, must, in both ultimate and proximate analysis, be measured before and after the operations indicated, and must be reduced to standard conditions.

The values to be determined are, the volume of the gas, its absolute temperature, and its pressure. These values are respectively designated by V, T, and P. Different methods of gas analysis have been devised which base on the determination of the one or the other of these values.

In Regnault's method, for instance, P is measured, in Orsat's process V is determined; where the analysis is effected by the eudiometer and the absorption tube, V, T, and P, are recorded.

Proximate Analysis.—The apparatus generally employed for proximate analysis consists of a combination of three tubes which are all in connection, but the communication between which can be entirely shut off by stopcocks. A measured volume of gaseous mixture is introduced into the so-called absorption-tube. There it is treated successively with different reagents to remove the various constituents it may contain; the gas is remeasured after treatment with each reagent, and its volume noted.

Thus, potassium hydrate removes carbon dioxide, sulphurous oxide and sulphuretted hydrogen; pyrogallate of potassium removes oxygen; bromine removes the olefiants, cuprous chloride removes carbon monoxide, etc.

If the gaseous mixture contains hydrogen, this will remain after removal of the constituents above named.

A known volume of the hydrogen is transferred to a tube provided with two platinum wires or foils, an excess of oxygen is introduced, the mixture is exploded, and the residual volume of the gas is measured.

From the data thus obtained, the percentage composition of the gaseous mixture is calculated.

EXAMPLE :	1. Volume of gas used	92.0 c. c.
	2. Volume after absorption of CO_2	89.0 c. c.
	3. Volume after absorption of CO	69.0 c. c.
	4. Volume taken for estimation of hydrogen	58.0 c. c.
	5. Volume after addition of air	93.0 c. c.
	6. Volume after combustion	75.0 c. c.

$$CO_2 = \begin{array}{r} 92.0 \\ -\ 89.0 \\ \hline 3.0 \text{ c. c.} \end{array}$$

$$\frac{3.0 \times 100}{92.0} = 3.26 \text{ per cent } CO_2.$$

$$CO = \begin{array}{r} 89.0 \\ -\ 69.0 \\ \hline 20.0 \end{array}$$

$$\frac{20 \times 100}{92} = 21.74 \text{ per cent CO.}$$

Contraction on combustion:

$$\begin{array}{r} 93.0 \\ 75.0 \\ \hline 18.0 \text{ c. c.} \end{array}$$

$$2 \text{ vols. } H_2 + 1 \text{ vol. } O_2 = 2 \text{ vols. } H_2O.$$

Two thirds of the contraction represents the volume of hydrogen present.

The volume of hydrogen taken, is 58.0 c. c., therefore:

$$\frac{18 \times 2}{3} = 12.0 \text{ c. c.}$$

$$\frac{12.0 \times 69.0 \times 100}{58.0 \times 92} = 15.52 \text{ per cent } H_2.$$

The percentage of nitrogen present is determined by adding the values calculated, and subtracting their sum from 100.

The gas analyzed has therefore the following composition:

CO_2 =	3.26	per cent.
CO =	21.74	"
H_2 =	15.52	"
N_2 =	59.48	"
	100.00	

Method of Explosions.—The composition of some gaseous mixtures can be effected entirely by the method of explosions, by what is termed, the indirect method.

An explosion of combustible gases causes a diminution of volume. This contraction, the volume of CO_2 produced, and the original volume of the gas employed, are the only data necessary to calculate the composition of a gaseous mixture in an analysis of this kind.

The contraction experienced by the different gases in combustion can be determined by experiment, or, it can be deduced from the law governing the combination by volumes. For instance:

In the case of H_2:

$$2 \text{ vols. } H_2 + 1 \text{ vol. } O_2 = 2 \text{ vols. } H_2O.$$

But, unless the tube is kept at a temperature above the boiling-point of water, the water-vapor condenses and the gas all disappears. Therefore in this special instance:

$$2 \text{ vols.} + 1 \text{ vol.} = 3 \text{ vols. become } 0 \text{ vol.}$$

The *loss* in volume experienced is therefore 3 volumes.

Two vols. of H_2 were employed. $\frac{3}{2} = 1.5$; therefore the contraction is 1.5 times as great as the unit volume of the gas, hydrogen, which was exploded.

In the case of CO:

$$2 \text{ vols. } CO + 1 \text{ vol. } O_2 = 2 \text{ vols. } CO_2,$$
$$\text{vols.} + 1 \text{ vol.} = 3 \text{ vols. become } 2 \text{ vols.}$$

The loss is therefore 1 volume. Dividing this loss by the number of volumes of the gas exploded, carbon monoxide, we have $1 \div 2 = 0.5$. The contraction therefore is $\frac{1}{2}$ the unit volume of the gas exploded.

In the case of CH_4:

$$1 \text{ vol. } CH_4 + 2 \text{ vols. } O_2 = 1 \text{ vol. } CO_2 + 2 \text{ vols. } H_2O.$$

1 vol. + 2 vols. = 3 vols. become 1 vol., for the 2 vols. water-vapor condense.

The loss is therefore 2 volumes, and the contraction is $2 \div 1 = 2$. Hence the contraction is twice as great as the original volume of the gas represented.

EXAMPLE:* If a mixture of hydrogen, carbon monoxide, and methane is to be analyzed, these gases can be respectively represented by x, y, and z.

If the original volume of the gas is designated by A, the contraction by C, and the amount of CO_2 by D, then

$$\begin{aligned} A &= x + y + z \\ C &= 1\tfrac{1}{2}x + \tfrac{1}{2}y + 2z \\ D &= y + z. \end{aligned}$$

The values of x, y, and z must be calculated.

To find x:

$$\begin{array}{lr} & x + y + z = A \\ & y + z = D \\ \hline (1) & x = A - D \end{array}$$

To find y:

$$\begin{array}{lrcl} & 4y + 4z &=& 4D \\ & 3x + y + 4z &=& 2C \\ \hline & -3x + 3y &=& -2C + 4D \\ & 3x &=& 3A - 3D \\ \hline & 3y &=& 3A - 2C + D \\ (2) & y &=& \dfrac{3A - 2C + D}{3}. \end{array}$$

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* From Sutton, Volumetric Analysis, 6th Ed., 1890.

To find z:

$$y + z = D$$

$$z = D - y$$

$$z = D - \frac{3A - 2C + D}{3}$$

$$(3) \qquad z = \frac{2C - 3A + 2D}{3}.$$

Substituting the values found by experiment in these three formulæ, which give the values of x, y, and z, respectively, the amounts of hydrogen, carbon monoxide, and methane represented by these letters are easily calculated.

The percentage composition of the gaseous mixture is ascertained by solving the following proportions:

$A : x :: 100$: per cent of H;
$A : y :: 100$: per cent of CO;
$A : z :: 100$: per cent of CH_4.

If the gas mixture contained nitrogen, this would be determined by exploding the residual gas, after removal of the CO_2, with an excess of hydrogen. The contraction observed divided by 3, would give the volume of oxygen in the residue, and this deducted from the residue, would yield the amount of nitrogen. If A represents the original gas, and n the amount of nitrogen it contains, the expression $A - n$ would have to be substituted for A in the equations cited.

Having ascertained the proximate constituents of a gaseous mixture, the amounts of the elements present, carbon, hydrogen, nitrogen, etc., can, of course, be very readily calculated.

CHAPTER IX.

THE PERIODIC LAW.

Introductory.—The fact that certain similarities exist between the properties of some of the elements, has been known for a long time, and attempts to find connections between the general properties of such elements and their respective atomic masses, date back to about the first quarter of this century.

Thus, Döbereiner, in 1829, noticed that in several instances an element possesses an atomic mass which is approximately the average of the atomic masses of two other elements which resemble it closely in their properties.

For instance, the atomic masses of calcium, barium, and strontium are, respectively, 40, 136.9, and 87, the latter number being approximately one half of the sum of the other two. Again, bromine has an atomic mass of 80, about one half of the sum of the atomic masses of chlorine 35.5, and of iodine 126.5.

Döbereiner further found, that in some cases three elements, which have analogous properties, possess atomic masses which are almost identical. Such groups are formed, for instance, by iron, cobalt, and nickel, and by platinum, osmium, and iridium.

This investigator hoped that a systematic classification of the elements might be established on this basis, but a realizing of this wish was not possible, until careful analysis had furnished accurate determinations of the atomic masses.

Gmelin, Dumas, Cooke, Pettenkofer, Kremers, Odling, and

Gladstone, among others, worked to the attainment of this end, but the periodic law, as it is now established, is due chiefly to the labors of Newlands, Mendeléeff, and Lothar Meyer.

The first communication of Newlands, "On Relations among the Equivalents," appeared early in 1863.*

In 1864 a list of the elements then known, was by him given in the order of their atomic masses—the first list of the kind ever published.

Mendeléeff first enunciated the periodic law in his work on chemistry, in 1869, and Lothar Meyer's announcement of it was made, independently, in the same year.

The Periodic Law.—The law is thus stated : The properties of the elements are periodic functions of their atomic masses.

A phenomenon is periodic when it recurs at definite intervals, while the conditioning circumstances vary continuously. In this case, the variable is the atomic mass, which increases constantly, while the properties of the elements recur at stated intervals.

Although the dependence of all the physical and chemical properties of the elements upon their atomic mass, has not yet been clearly demonstrated, still, the numerous intimate relations already firmly established, mark the Periodic Law as one of the most important laws of chemistry.

As the manner of grouping the elements adopted by Newlands, Mendeléeff, and Lothar Meyer is not the same, although of course in each instance the elements are placed in the order of their atomic masses, all three arrangements are here given.

Newlands' Table† was first published in the *Chemical News* in 1875, where he stated: "Elements belonging to the

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* *Chemical News*, Vol. VII, p. 70, Feb. 7, 1863.

† On the Discovery of the Periodic Law, and on Relations among the Atomic Weights. John A. R. Newlands.

same group stand to each other in a relation similar to that between the extremes of one or more octaves in music. Thus, if we commence counting at lithium, calling it 1, sodium will be 8 and potassium 15, and so on. To save the trouble of counting in each individual case, and also to render the relationship obvious at a glance, it is convenient to adopt a horizontal arrangement."

Newlands' Table.

Elements in Order of Atomic Weight.

HORIZONTAL ARRANGEMENT.

1.	2.	3.	4.	5.	6.	7.	8.
a.....	Li 7.0	Na 23.0	K 39.1	......	Cu 63.4	Rb 85.4	......
b.....	Be 9.4	Mg 24.0	Ca 40.0	......	Zn 65.2	Sr 87.6	......
c.....	B 11.0	Al 27.4	......	Fe 56.0	......	I 88.0?	......
d.....	C 12.0	Si 28.0	Ti 50.0	......	......	Zr 89.6	Rh 104.4
e.....	N 14.0	P 31.0	V 51.2	.....	As 75.0	Nb 94.0	Ru 104.4
f.	O 16.0	S 32.0	Cr 52.2	Ni 58.8	Se 79.4	Mo 96.0	Pd 106.6
g H 1.	F 19.0	Cl 35.5	Mn 55.0	Co 58.8	Br 80.0	......	......

1.	9.	10.	11	12.	13.	14.	15	16.
a.....	Ag 108	Cs 133.0	..	....	Au 197.0	......	..	......
b.....	Cd 112	Ba 137.0	..	....	......	Hg 200.0	..	......
c.....	In 113.4	Di 138.0?	..	Er 178.0?	......	Te 203.6	..	......
d.....	Sn 118.0	Ce 140.0?	..	La 180.0?	Pt 197.4	Pb 207.0	..	......
e.....	Sb 122.0	....	..	Ta 182.0	Ir 198.0	Bi 210.0	..	Th 235.0
f.....	Te 128.0	....	..	W 184.0	Os 199.2	......	..	......
g.....	I* 127.0	....	..	....	....	......	.	U 240.0

NOTE.—"The quantivalence of the elements on the different horizontal lines is usually as follows:

Line a, Monads.
" b, Dyads.
" c, Triads.
Line d, Tetrads.
" e, Triads (or Pentads).
" f, Dyads (or Hexads).
Line g, Monads (or Heptads)."

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* ?—F. G. W.

Mendeléeff's Table* which shows the distribution of the elements in periods, shows two small periods, each containing seven elements, and five, so-called, large periods.

The elements at the commencement of each series are base-forming, those at the end of the series are acid-forming elements. This is especially marked in the two short periods. The transition from base to acid forming elements is gradual, the intermediate members forming oxides, which are neither pronouncedly basic nor acid.

There is a striking contrast in the chemical properties between the last member of any given series and the first member of the series next following.

Mendeleeff's Table.

The Atomic Weights of the Elements.

DISTRIBUTION OF THE ELEMENTS IN PERIODS.

Groups.	Higher Salt-forming Oxides.	Typical or 1st Small Period.	Large Periods.				
			1st.	2d.	3d.	4th.	5th.
I..	R_2O	Li = 7	K 39	Rb 85	Cs 133	......	......
II..	RO	Be = 9	Ca 40	Sr 87	Ba 137	......	......
III..	R_2O_3	B = 11	Sc 44	Y 89	La 138	Yb 173	......
IV..	RO_2	C = 12	Ti 48	Zr 90	Ce 140	......	Th 232
V..	R_2O_5	N = 14	V 51	Nb 94	......	Ta 182	......
VI..	RO_3	O = 16	Cr 52	Mo 96	......	W 184	Ur 240
VII..	R_2O_7	F = 19	Mn 55	......	......	......	......
VIII..	....	....	Fe 56	Ru 103	......	Os 191	......
	....	....	Co 58.5	Rh 104	......	Ir 193	......
	....	....	Ni 59	Pd 106	......	Pt 196	......
I..	R_2O	H = 1 Na = 23	Cu 63	Ag 108	......	Au 198	......
II..	RO	Mg = 24	Zn 65	Cd 112	......	Hg 200	......
III..	R_2O_3	Al = 27	Ga 70	In 113	......	Tl 204	......
IV..	RO_2	Si = 28	Ge 72	Sn 118	......	Pb 206	......
V..	R_2O_5	P = 31	As 75	Sb 120	......	Bi 208	......
VI..	RO_3	S = 32	Se 79	Te 125	......	......	......
VII..	R_2O_7	Cl = 35.5	Br 80	I 127	......	......	......
		2d Small Period.					

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* The Principles of Chemistry, by D. Mendeléeff. Translated from the Russian (Fifth Edition) by George Kamensky and A. J. Greenaway. London and New York, 1891.

Lothar Meyer's Table* shows the symbols of the elements written in the order of their atomic masses, but in horizontal rows.

Hydrogen being accepted as the unit of atomic mass, the first line is commenced by Li = 7.01, then comes Be = 9.08, and so on. Writing is continued in the same horizontal line until an element is reached, which resembles lithium in its chemical properties.

The symbol of this element, Na = 23.0 is placed under that of Li, and thus forms the beginning of the second line, which line ends with Cl = 35.37. K = 39.03 begins the third line, and the writing is continued in this manner, until the symbols of all of the elements have been noted in the order of their atomic masses.

If on the tabular scheme thus produced, horizontal lines be drawn under each line of symbols, and if vertical lines be drawn after each symbol, it will be seen, that the elements are divided into horizontal and into vertical rows. The former are termed series or periods, the latter, groups. The groups contain elements closely allied in their properties; for instance, Group I. consists of: Li, Na, K, Rb, Cs.

In the first two series, each of which consists of seven members, the two elements which fall into the same group, closely resemble each other; thus, for instance, Li and Na, C and Si, Fe and Cl.

The gaps which appear in all of these tables—where they are indicated by dots—will probably some day be filled by elements as yet undiscovered.

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* Outlines of Theoretical Chemistry, by Lothar Meyer. Translated by P. Phillips Bedson and W. Carleton Williams. London and New York, 1892.

Lothar Meyer's Table.

Natural System of the Elements.

HYDROGEN H = 1.

I.	II.	III.	IV.
Li 7.01	Be 9.08	B 10.9	C 11.97
Na 23.0	Mg 24.3	Al 27.04	Si 28.3
K 39.03	Ca 39.91	Sc 43.97	Ti 48.0
Cu 63.18	Zn 65.10	Ga 69.9	Ge 72.3
Rb 85.2	Sr 87.3	Y 88.9	Zr 90.4
Ag 107.66	Cd 111.7	In 113.6	Sn 118.8
Cs 132.7	Ba 136.9	La 138	Ce 139.9
....	....	Yb 172.6	....
Au 196.7	Hg 199.8	Tl 203.7	Pb 206.4
....	....	....	Th 232.0

V.	VI.	VII.	VIII.
N 14.01	O 15.96	F 19.06	....
P 30.96	S 31.98	Cl 35.37	....
V 51.1	Cr 52.45	Mn 54.8	Fe 55.88
As 74.9	Sc 78.87	Br 79.76	....
Nb 93.7	Mo 95.9	....	Ru 101.4
Sb 119.6	Te 125.0	I 126.54	....
....	....	....	....
Ta 182	W 183.6	....	Os 191
Bi 207.3	....	....	....
....	U 239.0	....	....

VIII.	
....	....
....	....
Co 58.6	Ni 50.6
....	....
Rh 102.7	Pd 106.35
....	....
....	....
Ir 192.3	Pt 194.3
....	....
....	....

Atomic Analogues.—Mendeléeff pointed out, that in many instances the value of any given property of an element is approximately the average of the values of the same property of the two elements which immediately adjoin it, either in the same series, or in the same group.

Thus, glancing at Lothar Meyer's table, it will be seen that the atomic mass of S = 31.98 is approximately the mean of the atomic mass of P = 30.96 and Cl = 35.37 which adjoin it on the right and left, and that it is also the average of the atomic mass of O = 15.96 and of Cr = 52.45 which are placed immediately above and below it in the scheme.

Four elements thus related, are termed *atomic analogues.*

Similar groups of analogues can be traced with reference to other properties of the elements.

Mendeléeff's Predictions.—Mendeléeff, from such considerations, predicted the existence and the properties of elements which were to fill the gaps existing between boron and yttrium, aluminium and indium, and, silicon and tin, respectively. These elements received from him the provisional names of eka-boron, eka-aluminium, and eka-silicon.

Gallium, discovered in 1875, proved to be the element whose existence and properties Mendeléeff had predicted as eka-aluminium; scandium, discovered in 1879, met the requirements claimed for eka-boron, and germanium, discovered in 1886, proved to have the atomic mass and the properties predicted for eka-silicon.

Importance of the Periodic Law.—A study of the elements when arranged in such systems according to the periodic law, has resulted not only in the prediction of the existence and the properties of elements as yet undiscovered, but has proved of value also in leading to the correction of several erroneous atomic mass values of some of the elements—of tellurium, of cæsium, and of indium, among others.

Graphic Curves.—Perhaps the best way of clearly bringing out the fact that the properties of the elements are periodic functions of their atomic masses, is to present these relations graphically, by means of curves.

Such curves are of value in affording an immediate and comprehensive view over a great number of data, in illustrating the co-ordination of different phenomena, and also in serving as a ready means for controlling the correctness of conclusions and inferences drawn from experiments.

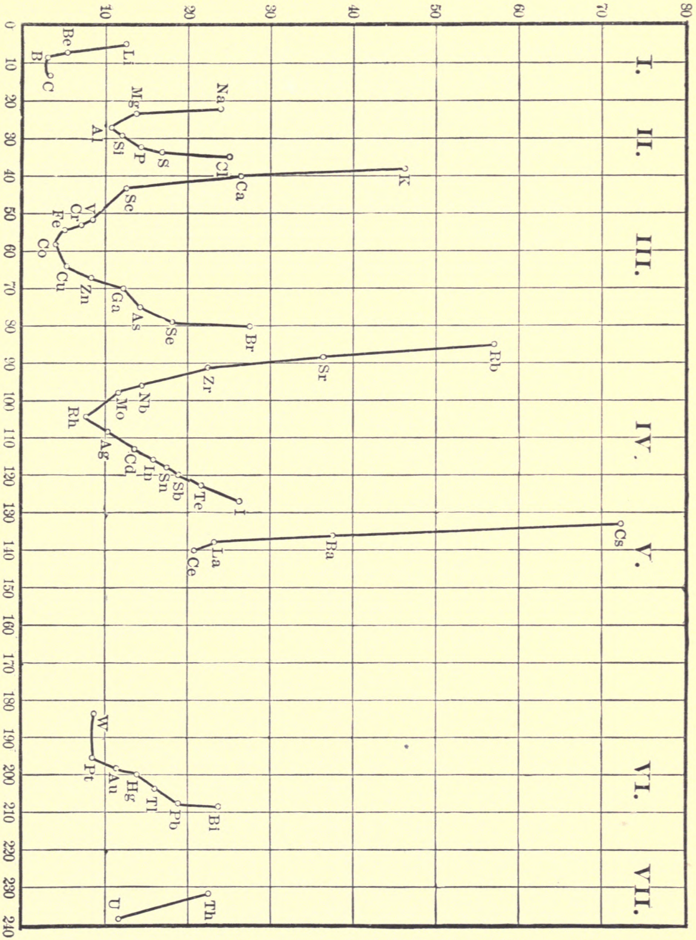
As was first shown by Lothar Meyer, the atomic volumes afford an excellent illustration of periodic variation.

The term *specific volume* expresses the volume occupied by the unit mass of a substance; this value multiplied by the atomic mass of an element, gives as the product a value termed, the *atomic volume.*

In the following cut the symbols of the elements are recorded on the horizontal line at distances from zero proportional to their atomic masses, and the atomic volumes are marked on the scale of the vertical line, according to their respective numerical value.

The curves which result on combining the consecutive points are irregular, but bear a certain resemblance to each other. Taking the curve as a whole, it will be found to consist of two kinds of curves, or periods, as they are called. The first two are short, and the others are long periods.

It will be seen, that the first element of each period is an alkali metal, and thus in general, similar positions in the different periods are held by elements similar in their chemical properties.


I.
II.
III.
IV.
V.
VI.
VII.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
10
20
30
40
50
60
70
80
Li
Be
B
C
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
V
Cr
Fe
Co
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Rh
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
W
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Periodicity of the Properties of Elements and Compounds.—Many of the chemical and physical properties of the elements are periodic, and the same holds true of the properties of their compounds.

Thus, the periodicity of valence, of the specific gravity in the solid state—as shown by a comparison of the atomic volumes, of the electro-chemical properties, of the melting-point, of the magnetic power, of the refractive power, of the conductivity for heat and electricity, of the toxic properties of the metals, etc., have all been carefully studied. The periodicity of the molecular volume of the oxides, as well as the acid and the basic properties of these compounds, must also be mentioned.

A tracing out of these different relations is most interesting, and although the periodic law cannot as yet give a logical explanation of all these phenomena, still it stands unquestioned, that it is one of the most far-reaching, if it be not, the most important law of chemistry.

CHAPTER X.

SOLUTIONS.

Definition.—Mixtures which are perfectly homogeneous, chemically as well as physically, and from which the components cannot be separated by mechanical means, are termed solutions. Sometimes they are also referred to as "physical mixtures," and this term is understood as embracing homogeneous gaseous mixtures, solutions, alloys, etc.

The state of aggregation of substances determines to a great extent their ability to form solutions, and perhaps the best way to point out the relations obtaining, will be to consider briefly the behavior of substances towards each other when in the gaseous, the liquid, and the solid condition.

Gases in Gases.—Gaseous mixtures afford the best opportunity for studying the behavior of solutions, because the existing conditions are most simple.

If the gases are so chosen, that no chemical action takes place between them, the ability to form solutions is unrestricted; this means, that they can intermingle and mix with one another in all proportions.

In such a mixture, each gas will retain to the fullest extent its original properties, and will exhibit the same in the same manner, as if it alone were present.

Thus, the pressure exerted by any gaseous mixture is equal to the sum of the pressures exerted by its individual components. That is to say, each gas, uninfluenced by the presence of the other gases, exercises the same pressure which it would exercise if it alone filled the entire space,—a fact already recognized by Dalton in 1802. This pressure is termed the partial pressure of the gas.

The power of a gaseous mixture to absorb light and to refract light, has likewise been shown to be in accordance with the law of addition, in virtue of which, any given property of a gaseous mixture is equal to the sum of that property of its components.

The reason why the laws governing solutions of gases in gases, are simple and easy of discernment, is found in the fact, that in the gaseous state the individual particles of matter are at a considerable mean distance from each other,—a distance sufficiently great to prevent the mutual action of the particles induced by close proximity.

Gases in Liquids.—With hardly an exception, all gases are soluble in all liquids, but the amount of different gases which liquids can dissolve, varies within very wide limits, and is dependent upon the nature of both the liquid and the gas concerned.

The amount of a gas dissolved by a liquid is generally expressed in terms of volume, and not in parts by weight.

"Coefficient of absorption" is the term used by Bunsen to denote the volume of a gas under standard conditions of temperature and pressure, absorbed by the unit volume of a given liquid under normal pressure.

Ostwald uses the expression "solubility of a gas," to denote the ratio of the volume of gas absorbed to the volume of the absorbing liquid, at any specified temperature and pressure.

Solutions of gases in liquids are divided into two groups:

(*a*) Those solutions from which the dissolved gas can be removed easily by decreasing the pressure or by increasing the temperature; and (*b*) those solutions which refuse to yield up all of the dissolved gas when subjected to the indicated changes in pressure and temperature; but in such instances a chemical change has most likely taken place, thus leaving the matter no longer a problem of simple solution.

Solutions of gases in liquids, belonging to the first of these two groups, act in obedience to the law of Henry, which holds, that: the quantity of a gas dissolved by a certain amount of a liquid, is proportional to the pressure of the gas.

Bearing in mind the fact that the volume of a gas is inversely as the pressure to which it is subjected, Henry's law can also be thus stated: A given amount of a liquid will always dissolve the same volume of a gas, irrespective of the pressure.

When a gaseous mixture is dissolved by a liquid, the quantity of each gas dissolved is proportional to its partial pressure; that is to say, in absorbing a gaseous mixture, the liquid absorbs each constituent of this mixture as if it alone were present, and exerted its own independent pressure.

Gases in Solids.—A well-known instance of a gas dissolved in solids (metals), is furnished by the absorption of hydrogen by palladium, iron, platinum, potassium, and sodium.

At a red heat, palladium will absorb about 935 times, platinum about 3.8 times, its own volume of hydrogen gas. Hydrogen has also been found absorbed—"occluded," as it is termed, in certain meteorites. The meteorite of Lenarto, for instance, when heated in vacuo yielded more than 2.5 times its own volume of this gas.

Liquids in Gases.—The tendency of liquids to pass into the gaseous condition, to evaporate, is closely allied to the facility with which liquids mingle with gases and form gaseous mixtures.

Dalton stated as the law obtaining in these cases: the vapor pressure of a liquid in a gas is the same as in a vacuum.

The accuracy of this has been questioned by Regnault and others, but recently, careful observations made on the behavior of water and ether, in vacuo and in air, showed the differences to be very slight—as a rule, not exceeding one per cent.

Liquids in Liquids.—In studying the solution of liquids in liquids, a division into three groups is generally made.

Group I. embraces those liquids which readily mix with each other in all proportions; water and alcohol, for instance, will serve as an illustration of this type.

But the solubility of liquids is materially affected by the temperature; and certain liquids—for example, water and aniline, which at the ordinary temperature will dissolve one another but very slightly—will, if heated up to nearly 170°, mix together in all proportions. Likewise, phenol and water become miscible in all proportions when a temperature of 80° is reached.

Generally speaking, the properties of mixtures of liquids are not additive, as was found to be the case in gaseous mixtures. This means, that any given property of a mixture of liquids is not necessarily equal to the sum of that property of its constituents.

Thus, the volume of a mixture of two or more liquids is not necessarily equal to the sum of the volumes of the component liquids: in most instances it is smaller, than this sum.

A satisfactory explanation of this has not yet been advanced; for, although changes of temperature frequently occur on the mutual solution of liquids, such changes may consist in an increase or in a decrease of temperature, and no definite connection between changes in temperature and changes in the volume of the mixtures has yet been traced.

Group II. consists of liquids which dissolve each other, but only in restricted proportions.

An example of this type is afforded by water and ether. If a mixture of these two liquids is made, then, when separation into layers is brought about, the water solution will contain 10% of ether, and the layer of ether will be found to hold 3% of water.

Group III. is reserved for those liquids which exercise practically no solvent action on each other. There are even at present very few liquids which can be placed in this group, and it seems likely, that improved methods of analysis, i.e., the power of determining very minute quantities of certain substances, would transfer to the second group all liquids now classed in this division.

Liquids in Solids.—An instance of the solution of a liquid in solids is afforded by the mixture of mercury with the solid metals. Mixtures of this kind are termed amalgams. Amalgams may be solids—they even frequently occur in the crystalline condition; or they may be liquids, in which case they contain a considerable excess of mercury.

As a rule, amalgams are unstable, and some can be decomposed by subjecting them merely to high pressure.

The formation of amalgams is attended in some instances by the evolution, in others by the absorption, of heat. As to whether amalgams should be considered as chemical compounds or as physical mixtures, the preponderance of evidence seems to favor the latter view, although the existence of definite compounds of mercury with some metals is unquestioned.

Solids in Gases.—Ostwald considers it justifiable to speak of the solution of solids in gases, "inasmuch as certain solids can be evaporated without going through the liquid condition." *

As yet the law of these phenomena has not been determined by experiment, but Ostwald presumes that Dalton's law will be found to hold good also for solutions of solids in gases.

Solids in Liquids.—The solution of solids in liquids is the most common, as well as the most important instance of solutions to be considered.

A solid soluble in a liquid will dissolve if it be merely left in contact with the solvent, but solution will in most cases be

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* Ostwald, W., Solutions, 1891 ; translated by M. M. Pattison Muir.

materially hastened if solid and solvent are well stirred or shaken together.

When a solvent refuses to absorb any more of a solid, the solution is said to be saturated with respect to that solid. In other words, a solution is saturated, when at any given temperature the solvent has absorbed the maximum amount of a solid which it can normally hold in solution at that temperature.

Under certain conditions however, solutions can be made to contain more than the quantity above referred to, and in that case they are said to be supersaturated; but such supersaturated solutions can be formed by all soluble bodies, and this condition must not be considered as exceptional.

The fundamental law governing the behavior of solids going into solution in liquids, is analogous to that which is valid for vapor-pressures.

The influence which pressure exerts on the solubility of substances has been much studied.

Möller and Sorby demonstrated that a change of pressure affects the solubility independently of a change of temperature. Recent investigations have shown, that although an increase of pressure generally conditions an increase of solubility, yet, at very high pressures a decrease of solubility is induced.

The manner in which changes in temperature influence solubility was already examined into by Gay-Lussac in the first quarter of this century, and since that time this problem has occupied the attention of several investigators.

As a rule, solubility increases with increasing temperature, and usually the solubility increases faster than the temperature increases. However, there are substances—for instance, some of the salts of calcium—the solubility of which is less at higher than at lower temperatures.

When a solid is dissolved in a liquid, generally speaking, a diminution of volume occurs. The amount of this diminution is determined by the ratio between the solvent and the solid dissolved; for a given amount of solid, the contraction is the greater, the greater the amount of solvent employed.

Solids in Solids.—Mixtures resulting from the permanent union of two or more metals which are solids at the ordinary temperature and pressure, are termed alloys.

Alloys are usually prepared by the aid of heat, but some alloys, of certain soft metals, can be made by pressure alone, and without elevation of temperature.

Whether alloys are true chemical compounds, or whether they are to be regarded as solutions of metals in each other, has long been a mooted question.

Definite compounds of metals in definite proportions by weight, undoubtedly do exist. It is, however, difficult to isolate these compounds, as they seem to dissolve in all proportions in the melted metals; and, as a rule, it appears that alloys are mixtures of definite compounds with an excess of one or more metals.

This view seems to be borne out by the fact that alloys preserve, more or less, some characteristics of their constituents.

Solutions of solids in solids do not, however, necessarily exhibit an additive character in their properties. The melting-points are usually lowered, the average density is increased. In certain alloys the conducting power for electricity is proportional to the relative volume of the components; in other alloys this is not the case. In many instances the volume of an alloy is less than the sum of the volumes of its components; in other instances the reverse is true.

Dilute Solutions.—A condition analogous to that obtaining in the gaseous state, can be produced by causing a substance—gaseous, liquid, or solid—to enter into contact with a liquid solvent, with which solvent said substance will form a homogeneous mixture, arranging the conditions so that the solvent will be present in considerable excess.

Such a solution is termed dilute. It is evident that in such a solution the particles of the dissolved substance will be widely separated from one another, and the behavior of substances when in a state of dilute solution, closely resembles the behavior of gaseous mixtures.

When two solutions of the same substance, but of different concentrations, are placed in contact, the two solutions will mingle with each other, and their movement will continue until the composition of the entire solution is homogeneous.

If this intermingling of the solutions is interfered with by the insertion of a membrane or of some other partition which will permit the passage of the solvent but not of the dissolved substance, then the latter will exert a pressure on the obstructing partition. This pressure is spoken of as the osmotic pressure, and is undoubtedly produced by the dissolved substance, for the solvent can pass freely through the partition, and moreover, an increase in the amount of the dissolved substance is accompanied by a proportionate increase of pressure on the partition. This power of movement is inherent in the particles of the dissolved substance, and it is merely rendered apparent by its action on the partition.

The phenomena which are caused by the action of this force in the particles of dissolved substances are termed osmotic or pressure phenomena; the movements alluded to are spoken of as the phenomena of diffusion. Osmose and diffusion play a very important part in nature.

Osmotic Pressure.—The conditions which are of special importance in studying the gaseous condition are the volume, the temperature, and the tension under which gases exist.

In dilute solutions, the first two conditions are determined by the volume and the temperature of the solvent, whereas, corresponding to the tension of gases, solutions exhibit the so-called osmotic pressure.

As enunciated by Van't Hoff, this osmotic pressure is independent of the nature of the solvent, and, in dilute solutions, is subject to the laws obeyed by gases—the laws of Boyle, Charles, and Avogadro.

Thus, for instance, for constant volume, osmotic pressure is proportional to absolute temperature, and, for all gases and vapors which dissolve in a solvent in amounts proportionate to their pressure, the osmotic pressure is equal to the corresponding gas-pressure.

A careful consideration of most copious experimental data has led to the conclusion, that the osmotic pressure of a substance in solution is equivalent to the gaseous pressure which would be observed, provided the solvent were removed and the dissolved substance, in the gaseous condition, were made to occupy the identical space.

This fact is of great practical importance, because, as already explained in the chapter on the determination of molecular mass, it permits the molecular mass determination of substances, the vapor density of which cannot be ascertained.

This peculiar relation between osmotic pressure and molecular mass, obtained in a purely empirical manner, called for an explanatory hypothesis.

Such an hypothesis was advanced by Van't Hoff, and it is practically an enlargement of Avogadro's Law, namely:

Solutions of identical osmotic pressure, termed isosmotic or isotonic solutions, contain at a given temperature, in equal volume, the identical number of molecules of dissolved substance; moreover, this number of molecules is the same as would be contained in the identical volume of a perfect gas, at the same temperature and pressure.

Measurement of Osmotic Pressure.—Several methods have been devised for the direct measurement of osmotic pressure.

Thus, Pfeffer placed a clay cell filled with a sugar solution, to which a little sulphate of copper had been added, into a dilute solution of ferrocyanide of potassium. This resulted in the deposition of a thin membrane of ferrocyanide of copper in the interior of the cell, a deposit which possesses the peculiarity of permitting water to pass through it, but which prevents the passage of many substances soluble in water, cane-sugar for instance.

The sugar molecules are thus prevented from escaping, and if cell and contents are placed into a vessel with water, the latter, in obedience to the laws of diffusion, will permeate the membrane of ferrocyanide of copper, and, entering the cell, will increase the volume of the sugar solution. If the cell be provided with a mercury manometer, the osmotic pressure can be directly ascertained, or if, instead of having this attachment, a tube is inserted in the cell, the sugar solution will rise in this tube, and the height to which the solution will rise above the level of the liquid in the cell will serve as a measure of the intensity of the osmotic pressure of the solution.

From Pfeffer's determinations many most interesting data were obtained. Thus, for instance, he found that the osmotic pressure is dependent to a very great extent on the nature of the dissolved substance; solutions of different substances of equal concentration produced very different, and some of them, very great pressures. For instance, a 1½ per cent solution of potassium nitrate produced a pressure of over three atmospheres.

But in most cases, it is a matter of extreme difficulty to measure osmotic pressures directly, and various methods have been devised to obtain the result desired, in an indirect manner.

All of these latter methods base upon a measurement of the amount of work which must be done in order to effect a separation of the solvent and the substance dissolved. For the osmotic pressure is a direct measure of this work, and therefore, if the latter be known, the former can be readily ascertained.

Among the principal methods resorted to to effect this separation of the solvent and of the substance dissolved, crystallization, evaporation, and selective solubility are perhaps most frequently employed. As each of these methods can be used in two ways, i.e., as either the solvent can be removed from the dissolved substance, or as the reverse can be effected, this practically opens up six distinct ways of indirectly determining osmotic pressure.

Diffusion.—As has been previously stated, the power of movement is inherent in the particles of a dissolved substance. In virtue of this property when two liquids of unequal concentration are placed in contact, they will mix with each other until a perfectly homogeneous solution is produced. This process is termed diffusion, and is a manifestation of osmotic pressure.

Graham, about the middle of this century, was the first to thoroughly investigate this matter, and in 1855 Fick advanced the theory that, " the quantity of a salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near one another." The truth of this statement was demonstrated by an investigation made by H. F. Weber twenty-four years later.

Graham, in his investigations, found that there is a very marked difference in the speed with which the particles of different substances move through water. To those substances which diffuse relatively fast and which generally occur in the crystalline form, he gave the name *crystalloids,* while those substances which diffuse slowly, and which usually are amorphous, were by him termed *colloids.*

Colloidal substances permit the passage of crystalloids, but are usually impervious to other colloids.

By inserting a membrane of some colloid between pure water on the one hand and a mixture of colloids and crystalloids on the other, a more or less perfect separation of the colloids and the crystalloids can be effected, because the latter will readily pass through the membrane and the colloids will not. The process of effecting a separation in this manner is termed dialysis—parchment-paper is usually the substance used as a membrane.

Even the brief outline sketch given in these pages of the laws of solutions and of the relations obtaining among them, will indicate the great importance which attaches to this department of theoretical chemistry; it is undoubtedly along these lines that great advances will be made in the near future.

CHAPTER XI.

ENERGY—CHEMICAL AFFINITY.

Introductory.—Associated with matter is energy, and, like matter, energy is indestructible.

Energy is the *cause* of all changes, of all transformations in the universe, and is perhaps best defined as: the capacity of doing work, of overcoming resistance.

Every particle of matter in space is in a determinate position with reference to other particles of matter. Continuous change of position is termed motion, and all energy is regarded as primarily due to the motion of matter.

Varying with the kind of motion, energy appears in various forms, as: heat, light, sound, as electrical, or as chemical energy.

These forms of energy are to a great extent mutually convertible, and convertible without loss.

Manifestations of energy are frequently referred to as forces, and as all energy is regarded as due to the motion of matter, force may be defined as: any cause that tends to produce, change, or destroy motion.

As energy is the cause of all change, many phenomena in nature are conventionally ascribed to the action of certain forces. Thus, the falling of bodies towards the surface of the earth is ascribed to the force of gravity; the combustion of a fuel, to the force of chemical affinity.

Measurement of Force.—In order to compare the magnitude of forces, it is necessary to effect their measurement, and in order that this may be done, some standard of measure, some unit of force must be adopted.

Forces are equal when they can produce the same acceleration on the same mass or on equal masses, and therefore a force may be measured by comparing it with the gravity of some known mass of matter.

THE GRAVITY UNIT OF FORCE is the gravity of any unit of mass, which unit of mass may of course be selected at pleasure.

The attraction exerted by the earth upon a given mass is variable; it varies according to the position of the mass on the earth's surface—with the latitude. Thus, at the sea-level, one gramme is drawn towards the earth with a velocity of:

978.1 centimetres per second, if at the equator,
980.6 " " " , " " latitude 45°,
983.1 " " " , " " the pole.

The gravity unit of force is hence a variable value.

THE ABSOLUTE UNIT OF FORCE is another unit by which force is measured. This unit represents the force that, acting during the unit of time on the unit of mass produces the unit of velocity.

Different absolute units of force can be constructed, based on different units of time, length and mass.

In science, the absolute or kinetic unit of force now almost universally adopted, is based, on the centimetre as the unit of length, on the gramme as the unit of mass, and on the second as the unit of time. This system of measurement is called the centimetre-gramme-second system, and is usually designated as the C. G. S. system.

The absolute unit of force in the C. G. S. system, is called the *dyne*. The dyne is the force that, acting on a mass of one gramme for one second produces a velocity of one centimetre per second.

RELATION BETWEEN GRAVITY UNITS AND ABSOLUTE UNITS.—Gravity units are easily transformed into absolute units. It has already been stated, that in latitude 45°, one gramme is drawn to the earth with a velocity of 980.6 centimetres per second. A dyne has been defined as imparting a velocity of one centimetre per second to a mass of one gramme, therefore, the weight of one gramme is equal to 980.6 dynes in latitude 45°, at the sea-level.

Measurement of Energy.—Energy is measured by the work which it can accomplish. The units selected for such measurement are:

a. The gravity unit.

b. The absolute unit.

THE GRAVITY UNIT OF WORK.—The gravity-unit usually adopted, is the kilogramme-metre. It represents the work done in raising one kilogramme vertically through the height of one metre.

THE ABSOLUTE UNIT OF WORK.—The absolute unit of work and in consequence, of energy, adopted in science, is the erg.

The erg represents the work done in moving a body, free to move, one centimetre against a force of one dyne.

Thus, the work done in lifting one gramme one centimetre vertically against the force of gravity, in latitude 45°, is equal to 980.6 ergs, for one gramme = 980.6 dynes in latitude 45°. And again, in raising a body weighing 20 dynes vertically through a height of 50 centimetres 20 × 50, i.e. 1,000 ergs of work are done.

The amount of kinetic energy possessed by matter depends upon the mass of this matter and upon its velocity.

If, m denotes the mass.

" v " " velocity with which m is moving, then:

$$\text{Kinetic Energy} = \tfrac{1}{2}mv^2.$$

The answer obtained, is of course in terms of the erg.

The Law of the Conservation of Energy—states, that the sum of all the various energies in the universe is a constant quantity.

The proof that matter is indestructible, can easily be given by quantitative chemical experiments, but the principle of the conservation of energy does not admit of such direct demonstration. The truth of this law can however be readily proven by indirect evidence.

For, if a law is true, then the prediction of certain results under certain conditions, must be possible, and in the case of this law of the conservation of energy, all tests ever made in this manner, have affirmed its correctness. Thus, for instance, Joule furnished the experimental demonstration of the law according to which work can be transformed into heat,—practically a proof of the law of the conservation of energy.

Chemical Affinity.

Introductory.—The one manifestation of energy which is of the greatest importance in chemistry, is the force of chemical affinity. Attraction is one of the universal attributes of matter, but according to the conditions under which it is exercised, for instance, whether at measurable or at inappreciable distances, whether between similar or between dissimilar particles or masses of matter, its action is designated by various terms.

Thus, gravitation or gravity is the name applied to attraction when exerted at measurable distances; the particles or masses of matter between which it is exercised, may be similar or dissimilar.

Attraction at inappreciable distances, when exerted between dissimilar particles is termed adhesion, between similar particles, cohesion.

An important point to be noted in this connection is, that the exercise of these various forms of attraction entails no change in the properties of the matter acted upon.

When the various forms of matter come to be studied from the chemical point of view, it is found, that matter is endowed with a property, in virtue of which, two or more dissimilar particles when brought into intimate contact, can give rise to other forms of matter, the properties of which can be, and generally are, entirely different from their own.

For instance, when sodium, a metal, is, under proper conditions, brought into contact with chlorine, a poisonous gas, sodium chloride is formed, a white salt, which not only is non-poisonous, but which is actually essential to the animal economy.

Again, when hydrochloric acid in aqueous solution, is allowed to act on calcium carbonate, a solid, there is formed, carbon dioxide, a gas, and chloride of calcium, a salt,—both substances with properties entirely different from the properties of the substances through the inter-action of which they were formed.

This peculiar property of matter has been designated by various terms, viz.: affinity, chemical affinity, heterogeneous affinity, chemical attraction, chemical action, molecular gravitation, elective gravitation, and chemism.

By exercise of chemical affinity, the physical, physiological and chemical properties of substances, either, or all, can be greatly influenced and affected.

Chemical affinity can be modified by mechanical action,—for instance, by pressure, agitation, or percussion. It can also be modified by the influence of light, by heat and by cold. Heat usually promotes, while cold exerts a retarding influence on chemical action.

Hypotheses regarding the Nature of Chemical Affinity.—Although nothing positive is known, even at the present day, concerning the nature of chemical affinity, yet a number of hypotheses concerning this subject have been advanced from time to time, and a brief review of these, in the order of their sequence, is not without interest.

The Greek philosophers sought to explain the difference of behavior between different substances, by assuming the existence of likes and dislikes, inherent in the various forms of matter.

Under influence of the teachings of Galileo, these views of chemical affinity were abandoned, and chemical affinity came to be regarded as due to the actual bringing into use of little hooks, points and projections, with which the ultimate particles of matter were conceived as endowed.

The next important change of view in regard to the nature of chemical affinity, was due to Sir Isaac Newton. He ascribed chemical affinity to the attractive action of small particles, but held, that the cause of chemical actions differed from that of general gravitation in several ways, principally, with respect to the influence that distance exercised on the result.

Bergman, Berthollet and others, deemed chemical affinity and gravitation to be forces of the same character, and claimed, that the seeming difference in their action must be ascribed solely to the difference in conditions under which these forces are exhibited.

Sir Humphry Davy, as early as 1807, expressed the belief, that the primary cause of electrical and chemical effects might be the same force. Electrical phenomena resulted, when this force was exerted between masses of matter, whereas chemical phenomena appeared, when this force was exercised between the smallest particles of substances.

A complete revolution in the ideas entertained with regard to the nature of chemical affinity, was introduced by Berzelius. Berzelius carefully studied the chemical effects produced by the electric current, and concluded electricity to be the primary cause of activity in all Nature. He conceived each atom as bearing a charge of electricity—both positive and negative; one of these charges predominated, and the dominant charge determined the electrical character of the atom. He regarded every compound as formed of two parts, one of which bore a charge of positive, the other of negative electricity.

The work of Joule and Mayer about the middle of this century, demonstrated the relationship between chemical affinity and various forms of energy, such as heat, electricity, etc. The mutual transmutability of these forces was shown, and thus the necessity of any further theorizing as to the nature of chemical affinity no longer existed.

In other words, chemical affinity is now generally regarded as one of the manifestations of energy, and it seems certain that it can, at least partially, be transformed into heat, light and electricity.

Measurement of Chemical Affinity.—Attempts to measure chemical affinity have been numerous and varied.

Laplace studied the action of acids upon compounds decomposable by acids, and expressed the view, that the intensity of the action of an acid was directly proportionate to its specific gravity.

Morveau, Gay-Lussac and others, believing, that adhesion must be regarded as the first stage of chemical affinity, by means of weights determined the force necessary to separate disks of uniform size, from various liquids. These disks were constructed of different materials, for instance, of metal, of glass, etc.

Wenzel, who commenced his investigations of the laws of chemical affinity in 1777, believed that the times required for the solution of metals in weak acids, afforded a means of measuring the strength of chemical affinity.

The fact, that different amounts of heat are required to effect the decomposition of different compounds, led Lavoisier and others to attempt a measurement of chemical affinity on this basis. For instance, it was noticed that FeS_2 is decomposed by a temperature of 816° C. and that sulphur volatilizes at 447° C.; the difference between these two values, was pronounced to be the numerical expression of the affinity between iron and sulphur.

This idea, advanced thus early in the history of chemical theory, may be regarded as the foreshadowing of a hypothesis concerning the nature of chemical affinity, which was brought forward at a much later date. This hypothesis holds, that chemical affinity consists in an attraction between the atoms, and that this attraction is dependent on variations in the potential energies of the atoms.

The thermal changes which accompany chemical reactions, have been regarded as indicative of the transformation of potential energy into kinetic energy, and attempts have been made to measure this transformation of energy by thermal methods. But thermal measurements, although they serve to throw some light on certain phases of the question, cannot lead to an understanding of the nature of chemical affinity, because the values yielded by the present methods of thermochemistry, express but the ultimate outcome of several chemical changes, the sum or the difference between the heats of decomposition and the heats of formation of the factors involved. Moreover, a portion only of chemical energy is transformed into heat, while other portions may appear in different forms. Von Helmholtz designates the former portion as *bound*, the latter, as *free energy*.

The theory, that the force acting between two different kinds of matter is analogous to the force acting between two masses of matter, had, in its day, a number of eminent men among its adherents. Reactions occurring between compounds, involving both decompositions and combinations, were ascribed to the action of two opposite forces, in which the stronger chemical affinity gained the victory.

This view found expression in the so-called "Tables of Affinity." In these, substances were arranged in the order of their supposed affinity for one another.

The earliest of these tables, of which the following is a specimen, were published by H. Geoffroy in 1718.

Table of Attraction.

SULPHURIC ACID.	POTASH.
Baryta	Sulphuric acid
Strontia	Nitric acid
Potash	Muriatic acid
Soda	Acetic acid
Lime	Carbonic acid
Ammonia	
Magnesia	

Bergman, in recognition of the fact, that chemical reactions vary according to the conditions under which they take place, in his tables of affinity, stated the behavior of each substance, when in aqueous solution, "in the wet way," and when at the temperature of fusion, "in the dry way." The following for instance, is the table he formulated for potash.

POTASH.

Wet Way.	Dry Way.
Sulphuric acid	Phosphoric acid
Nitric "	Boric "
Hydrochloric "	Arsenic "
Phosphoric "	Sulphuric "
Arsenic "	Nitric "
Acetic " etc.	Hydrochloric " etc.

Kirwan sought a solution of the problem in the different percentage amounts of the constituents of salts, i.e. of acids and bases. He formulated two general laws based on his observations. "The quantity of any base required to saturate a given quantity of any acid is *directly* as the affinities." And, "The quantity of any acid required to saturate any given quantity of a base, is *inversely* as the affinities."

Bethollet, whose views on chemical affinity have already been referred to, was the first to emphasize the important influence which is exercised by the *quantity* of the various factors taking part in any chemical reaction. Whether a certain metathesis takes place or not, depends not only on the so-called affinity, which the different factors may have for one another, but also on the relative amounts in which these factors are present.

To elucidate this particular aspect of the question, was the aim of the researches of two Norwegian scientists Guldberg and Waage, who enunciated a mathematical law with respect to the influence of mass.

They claimed, that the amount of a chemical change is proportional to the products of the active masses of the bodies concerned, and the coefficients of affinity of the reaction, of course presupposing elimination of secondary actions.

The term "coefficient of affinity" is best explained in their own words.* "In a simple decomposition of the form $AB + C = AC + B$, the formation of AC is chiefly brought about by the attraction between A and C; but there are also attractions between the other substances, and the *force* which causes the formation of AC is the *resultant* of all these attractions. This force may be regarded as constant for a definite temperature; we represent its amount by k, which we call the *coefficient of affinity* for the reaction in question.

In the same way, in the double decomposition, $AB + CD = AC + BD$, the *force* which causes the formation of the new substances, is a function of all the attractions between the bodies A, B, C, D, AB, CD, AC, and BD, and the *resultant force, k, is the coefficient of affinity* for the reaction."

Among other investigators whose labors have been directed to studying the influence of mass in chemical reactions, there should be mentioned H. Rose, Bunsen, Debus, Gladstone, and Ostwald.

The theory of Guldberg and Waage, which later on was formulated as a law by Van't Hoff, is practically identical with the views of Williamson and Pfaundler. L. Pfaundler, in 1867, was the first who applied hypotheses resting on a mathematical basis, to the views concerning the states of aggregation of matter, which had been advanced by Bernoulli, Joule and others.

Later on this theory was developed principally by Clausius and Maxwell, who assumed that substances consist of molecules, which are in continuous motion. It is claimed, that in the gaseous state, the velocity of the motion is directly proportional to the temperature, and inversely proportional to the

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* From M. M. P. Muir: A Treatise on the Principles of Chemistry.

square root of the molecular mass. There is supposed to be an oscillatory motion within the molecules, which in its intensity, stands in a definite relation to the motion of the molecules themselves. These views lend themselves readily to an explanation of partial reactions, of reversible reactions, and so forth.

The study and the measurement of chemical affinity by electrical methods has engaged the attention of many of the most eminent investigators, among them, of Faraday, Sir W. Thomson, Von Helmholtz and Ostwald.

The view is held, that in all solutions capable of conducting an electric current, the ions do not owe their existence to the action of the electric current, but that they exist as such, before the passage of the electrical current.

The electric conductivity of solutions is thus made to serve as a means for ascertaining the condition of the substances which are dissolved, for the number of dissociated molecules, i.e. the ions, determine, and are therefore a measure of, the quantity of electricity passing through a solution. The term "conductivity" represents the quantity of electricity which is conveyed in unit time by unit electromotive force.

The conductivity possessed by a solution which contains the molecular mass in grammes, of the electrolyte, is termed the *molecular conductivity*. This molecular conductivity increases with the temperature, and with the degree of dilution.

The conductivity of equivalent quantities, is called *equivalent conductivity*. As all equivalent ions transport the same quantity of electricity, and as the amount of electricity transported in a given time and by a given electromotive force, is directly proportionate to the number of moving ions and to the speed with which they move, to quote the words of Ostwald, "the equivalent conductivity is thus a direct measure of the velocity of migration of the ions."

As first enunciated by Kohlrausch, the molecular conductivity of an electrolyte is equal to the sum of the velocities of migration of the ions, or if:

m = molecular conductivity,
a = velocity of migration of anion,
c = velocity of migration of cathion,
x = the amount of the electrolyte dissociated into ions,

then,

$$m = x(a + c)$$

As can be shown by experiment, it is only on attaining infinite dilution, that the dissociation of an electrolyte into its ions becomes complete, and then:

$$m \infty = a + c$$

From these equations,

$$m = x(a + c)$$
$$m \infty = a + c$$

by division, there is found,

$$x = \frac{m}{m \infty}$$

This formula expresses the fact that, "the degree of dissociation of a dissolved electrolyte at any state of dilution is equal to the ratio of the molecular conductivity at this state, to the molecular conductivity at infinite dilution," and this value x, is made to serve as a measure of the chemical affinity of substances.

CHAPTER XII.

THERMAL RELATIONS—THERMOCHEMISTRY.

Introductory.—According to the theory of undulation, now generally accepted, heat is caused by the oscillatory motion of molecules. It is a form of energy, and is supposed to be transmitted through the intervention of an imponderable medium termed ether, which is assumed to completely pervade all space, that between molecules included.

Temperature.—The term temperature is given to that portion of heat, which can be perceived by the senses.

Variations in temperature are appreciable to the sense of touch; the extremes of the sensations experienced, are termed heat and cold. The sense of touch furnishes, however, only a relative indication of the temperature of a body, that is to say, through this sense of touch it can only be determined whether a substance is more warm or less warm than some other substance.

To ascertain the temperature of a body, resort is had to the physical action of heat on substances. As a rule, the expansion of substances caused by heat is measured and the value found is expressed in terms of some arbitrary unit.

Temperatures from about -40° to about $+340^\circ$ C. are usually registered by means of thermometers. The medium selected for use in thermometers is generally mercury, because this metal expands quite uniformly throughout the range indicated. Very high temperatures are measured by various devices. Sometimes they are determined by measuring the expansion of gases; rings made of different metals and alloys, or cones constructed of fire-clay, the fusing points of which are known, are frequently made use of for the purpose.

Although temperature must not be confounded with quantity of heat, yet temperature can be made to serve as a basis for the measurement of heat quantity, because it always requires the same amount of heat to raise the temperature of a given amount of a substance from one determined point to another.

Heat Units.—In order to measure amounts of heat, some thermal unit has to be selected in terms of which the values found, can be expressed.

The unit of heat adopted, is the amount of heat necessary to raise a unit mass of pure water through one degree of a thermometer-scale. Different values are in use, varying with the units of weight and with the thermometer-scale employed.

The unit of heat now generally accepted, is the amount of heat required to raise the temperature of 1 kilogramme of pure water from 0° to 1° C. For some purposes, the amount of heat required to raise the temperature of 1 gramme of water from 0° to 1° C. is adopted as unit. In these pages the term kilogramme-calorie (k. c.) will be used to denote the former, and the term gramme-calorie (g. c.) to designate the latter value.

The temperature of the water chosen as the standard temperature, is sometimes 4° C., sometimes, some other temperature more convenient for the purposes of the work undertaken, but, whatever the value taken, according to this method, a quantity of heat is measured by the quantity of water at a selected temperature which that quantity of heat would raise one degree in temperature.

Mechanical Equivalent of Heat.—The mechanical equivalent of heat is 423.99 kilogramme-metres. This means, that the energy, in form of heat, which is required to raise the temperature of one kilogramme of water from 0° to 1° C. can perform work equivalent to raising the weight of 1 kilogramme through a height of 423.99 metres.

Latent Heat.—When matter is caused to pass from the solid to the liquid state, or, from the liquid to the gaseous state, a certain amount of heat is absorbed, which is not indicated by the thermometer. This heat is called *latent heat*, and it may be defined as: The amount of heat required to effect a change of state of a body without affecting its temperature.

The latent heat of liquefaction is the amount of heat necessary to convert a substance from the solid into the liquid state, without sensibly affecting the thermometer. Thus, the latent heat of water is between 79 and 80, i.e., it will require between 79 and 80 heat-units to convert 1 kilogramme of ice at 0° C. into water at 0° C. In reversing the process, i.e. converting the water again into ice, the above-mentioned number of heat-units are again set free.

The latent heat of vaporization is the amount of heat necessary to convert a substance from the liquid to the gaseous state, without sensibly affecting the thermometer. Thus, the latent heat of steam is 537. This means, that 1 kilogramme of water at 100° C. absorbs 537 heat-units in its transformation into steam exhibiting a temperature of 100° C. In condensing steam into water, all of the heat-units previously absorbed are again yielded.

Specific Heat.—The *specific heat* of a body, previously referred to in connection with the determination of atomic masses, is the ratio of the amount of heat required to raise a given weight of a body one degree in temperature, compared to the amount of heat required to raise the same weight of water, one degree in temperature.

Determination of Specific Heat.—In the determination of specific heat values, three methods are principally used.

These are:

1. The method of the ice calorimeter.
2. The method of mixtures.
3. The time method.

1. THE METHOD OF THE ICE CALORIMETER.—In this method, a known weight of the substance is heated to a certain temperature. This temperature is noted, and then the substance is surrounded by dry ice at 0° C., and allowed to remain in contact with this ice until the temperature of the substance has fallen to 0° C. The amount of water formed by the partial melting of the ice is weighed, and the calculation is based on the latent heat of liquefaction of ice.

Of course proper precautions must be taken in all such experiments, to avoid as much as possible loss of heat by radiation, conduction, etc., so that all the heat lost by the substance may be considered to have been absorbed by the ice. In these experiments the data required, are:

1. Weight of the substance.
2. Initial temperature of the substance.
3. Weight of the water formed.

The substance will have lost:

$$(1) \times (2) \times \text{specific heat}$$

The water will have gained:

$$(3) \times 79.25^*$$

Since, according to the conditions of the experiment, all that has been gained in heat by the one substance has been lost by the other, these two quantities must be equal to each other, and as a result, we have an algebraic equation in which the specific heat sought is the only unknown quantity.

EXAMPLE:

Weight of a mass of nickel....	145.9 gms.
Initial temperature of the nickel...........	500° C.
Weight of water formed..................	100 gms.

The nickel has therefore yielded in heat-units 0.1459 × 500 × specific heat of Ni., and the ice has absorbed, in heat-units: 0.100 × 79.25. Therefore,

$$0.1459 \times 500 \times \text{specific heat of Ni} = 0.100 \times 79.25$$

$$\text{Specific heat of nickel} = \frac{7.925}{72.95} = 0.10863.$$

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*Accepting this as the latent heat of water.

2. THE METHOD OF MIXTURES.—A known weight of the body whose specific heat is to be determined, is mixed with a known weight of water or of some other substance, the specific heat of which is known. The temperatures of the two components are noted at the moment of mixture, and the temperature of the mixture is taken after thermal equilibrium has been established, that is, when both components have attained the same temperature. The necessary data are:

1. Weight of the substance, the specific heat of which is to be determined.
2. Temperature of this substance before mixture.
3. Weight of the substance, the specific heat of which is known.
4. Specific heat of this substance.
5. Temperature of this substance before mixture.
6. Temperature of the mixture.

The difference between (6) and (5) gives the change in temperature of the substance whose specific heat is known; the difference between (6) and (2) is the change experienced by the substance experimented on. Having obtained these values, the rest of the calculation is made as in the preceding instance.

This method is used principally to determine the specific heat of liquids, but it can also be employed to determine the specific heat of solids, as shown in the following example.

EXAMPLE :	Weight of a piece of zinc............	2 kilogrammes.
	Initial temperature of the zinc........	150° C.
	Weight of water used...	3 kilogrammes.
	Specific heat of water................	1.
	Initial temperature of the water.......	10° C.
	Final temperature of the mixture......	18.4° C.

The zinc has lost:

$$2 \times (150\text{–}18.4) \times \text{specific heat of Zn.}$$

The water has gained:

$$3 \times (18.4-10) \times 1.$$

Therefore,

$$\text{Specific heat of zinc} = \frac{25.2}{263.2} = 0.0957.$$

The ice calorimeter may evidently be regarded as a special application of the method of mixtures.

3. THE TIME METHOD.—In this method, sometimes termed, the method of cooling, a known weight of the substance, the specific heat of which is to be determined, is heated to a certain temperature, and then allowed to cool. The time which it needs to cool down to a certain temperature, compared with the time required, under identical conditions, by a known weight of water, or some other substance of known specific heat, to cool to the same extent, is made the basis of the calculation; the times for identical weights being proportional to the specific heats.

The data required, are:

1. Weight of the substance *a*, the specific heat of which is to be determined.

2. Time in which this substance *a*, cools a stated number of degrees.

3. Weight of the substance *b*, the specific heat of which is known.

4. Specific heat of this substance *b*.

5. Time in which this substance *b*, cools to the same extent as *a*.

In making determinations by this method, equal volumes of the substances are taken, which differ in weight by amounts proportional to their respective specific gravities.

The method of calculation used in this method, is best illustrated by a problem.

Example: Determine the specific heat of turpentine.

Weight of turpentine........................ = 1.3 kilogrammes.
Time in which 1.3 kilogrammes of turpentine will cool from 25° to 5° C............ = 22 minutes, 9 seconds.
Weight of water.......................... = 1.5 kilogrammes.
Specific heat of water......... .... = 1.0.
Time in which 1.5 kilogrammes of water will cool from 25° to 5° C..................... = 60 minutes.

$$1.5 : 60 :: 1.3 : y$$

$$y = 52.$$

That is to say, $y = 52$ minutes. This is the time required for 1.3 kilogrammes of water to cool from 25° to 5° C. Hence:

Time for cooling of 1.3 kilogrammes of water : Time for cooling 1.3 kilogrammes of turpentine : : Sp. ht. of water : Sp. ht. of turpentine.

$$52 : 22.15 :: 1 : x$$

$$x = 0.426$$

Therefore, the specific heat of turpentine = 0.426.

Of course, if in place of water, any other substance is used, the specific heat of which is known, the corresponding values for this substance must be used in place of those given for water in the above example.

This method is the least accurate of the three here described, but is convenient of application in certain instances.

The specific heat of gases may be determined either under constant pressure, or under constant volume. The tables of these data usually bring the former values, unless the contrary is specified.

Combustion.—In the process of combustion, the energy which is liberated in the formation of the products of combustion, appears principally as heat. In instances of the perfect combustion of the ordinary fuels, these products are carbon dioxide and water.

Calorific Power.—The calorific power of a substance is the amount of heat, i.e. the number of heat-units, evolved by the combustion of one unit-weight of the substance. The gramme or the kilogramme is usually the unit weight selected.

CALORIFIC INTENSITY.—The calorific intensity is the maximum theoretical temperature to which the products of combustion are raised.

The calorific power of a substance is a constant value. It is immaterial whether the combustion proceeds rapidly or slowly, whether it is completed at once, or is achieved in several stages.

Calorific intensity however, is a value dependent, to a certain extent, on the conditions under which the combustion is effected.

Let:

$C.\ I.$ represent the calorific intensity,
$C.\ P.$ represent the calorific power,
S, S', S'', represent the specific heats of the products of combustion of one unit weight of the substance,
m, m', m'', represent the amounts by weight of the products of combustion of one unit weight of the substance.

Then:

$$C.\ I. = \frac{C.\ P.}{mS + S'm' + m''S'' + \dots}.$$

In this formula there are reckoned as the products of combustion, not only the carbon dioxide and the water produced, but also the nitrogen of the atmosphere—if the combustion takes place in air, and the mineral matter, the ash of the fuel, if it contains any, for heat is used in raising the temperature of these bodies.

If water is produced in any process of combustion, attention must be paid to the state, liquid or gaseous, in which it is obtained.

The calorific power of 1 kilogramme of hydrogen burned in oxygen is 34,462 kilogramme-calories. This value includes the latent heat given out on the condensation of the water-vapor to the liquid state, that is, during its change from steam at 100° C. to water at 100° C.

In ordinary combustions, the water remains in the gaseous state, therefore, if the calorific intensity of hydrogen is to be calculated from its calorific power, there must be deducted from the value above given, the latent heat of vaporization of the water formed.

EXAMPLES.

Calculation of Calorific Power.

The symbol of methyl alcohol is CH_3OH. It is required to calculate its calorific power.

The first step is the calculation of the percentage composition of the substance named.

$$\begin{array}{lcl}
C = 12 & \dfrac{12 \times 100}{32} & = 37.50 \text{ per cent.} \\[2ex]
H_4 = 4 & \dfrac{4 \times 100}{32} & = 12.50 \text{ `` ``} \\[2ex]
O = 16 & \dfrac{16 \times 100}{32} & = 50.00 \text{ `` ``} \\
\hline
32 & & 100.00
\end{array}$$

As the calorific power of combustibles is usually given for 1 kilogramme of the substance, the composition of methyl alcohol is expressed in parts per thousand, and is,

$$\begin{array}{l}
C = 375 \\
H = 125 \\
O = \underline{500} \\
\quad\; 1000
\end{array}$$

It is customary to assume all of the oxygen present in a combustible to be combined with hydrogen, and the first calculation made, is to ascertain how much of the hydrogen present is thus in combination with the oxygen in the form of water.*

$$\mathrm{O} : 2\mathrm{H} :: 500 : x$$
$$16 : 2 :: 500 : x$$
$$x = 62.50$$

Total amount of H present..................... = 125.0
H in combination with O...... .... = 62.5

H available as fuel .... = 62.5

The calorific power of 1000 grammes of carbon = 8080 heat-units, (k. c.)

Calorific power of 1000 grammes of hydrogen = 34,462 heat-units, (k. c.)

Therefore, the carbon present, 375 grammes, yield:

$$\frac{8080 \times 375}{1000} = 3030 \text{ heat-units, k. c.}$$

and the hydrogen present, available as fuel, 62.5 grammes, yield:

$$\frac{34,462 \times 62.5}{1000} = 2154 \text{ heat-units, k. c.}$$

3030
2154

Total, 5184 heat-units, k. c.

There must now be determined the total amount of water produced:

$$2\mathrm{H} : \mathrm{H_2O} :: 125 : x$$
$$2 : 18 :: 125 : x$$
$$x = 1125$$

This means, that 1125 grammes of H_2O are formed.

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* If there is not enough hydrogen to satisfy all of the oxygen, then a certain amount of the carbon is assumed to exist in combination with the oxygen, and only the balance of the carbon present is calculated as available for thermic effect.

1000 grammes of water absorb 537 heat units in passing into the gaseous condition, 1125 grammes absorb 604 heat units, (k. c.) for:

$$1000 : 1125 :: 537 : x$$

$$x = 604$$

Heat-units produced, (total)	5184 k. c.
Heat-units absorbed	604 "
Calorific power of CH_3OH	= 4580 k. c.

Calculation of Calorific Intensity.

Calculate the calorific intensity of ethyl alcohol, burned in oxygen.

The calorific power of ethyl alcohol (1 kilogramme) .... = 6850 kilogramme-calories.
Specific heat of steam.................... = 0.475
Specific heat of carbon dioxide.......... = 0.2164

The combustion of ethyl alcohol takes place according to the equation:

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$$

On the combustion of 1 kilogramme of C_2H_5OH, there are formed:

$$C_2H_5OH : 2CO_2 :: 1 : x$$

$$46 : 88 :: 1 : x$$

$$x = 1.913 \text{ kgs. } CO_2.$$

And:

$$C_2H_5OH : 3H_2O :: 1 : x$$

$$46 : 54 :: 1 : x$$

$$x = 1.227 \text{ kgs. } H_2O$$

The calorific intensity is calculated by application of the formula previously given:

$$\text{C. I.} = \frac{6850}{1.913 \times .2164 + 1.227 \times .475}$$

$$\text{C. I.} = \frac{6850}{.4139 + .5828} = \frac{6850}{.9967}$$

and the calorific intensity, of ethyl alcohol = 6872° C.

Thermochemistry.

Of all the forms in which energy is manifested, there is perhaps none of greater importance, and of more frequent occurrence, than that denoted as chemical energy. But notwithstanding this fact, unfortunately, no means are known whereby energy, appearing in this form, can be directly measured.

Chemical energy is however readily transformed into heat, and thermochemistry has for its object the measurement of chemical energy in thermal units ; the amount of heat liberated or absorbed in chemical processes, serving as a measure of the changes taking place in the chemical energy of the system or systems, involved in a given operation.

Methods Employed in Thermochemistry.—The apparatus used to make thermochemical determinations of course varies considerably, according to the nature of the determination to be made. Measurements which are to be made on substances in aqueous solutions, are conducted in a vessel termed a calorimeter ; these calorimeters are generally made of glass or of platinum.

If of metal, the sides of the calorimeter are made as thin as possible. Its capacity generally ranges from about five hundred to one thousand cubic centimetres ; its shape is usually cylindrical. This cylinder is provided with a very accurate thermometer, graduated in fiftieths of a degree. This allows readings to be made accurately to $\frac{1}{100}$ of a degree, and, when read by a telescope, permits estimations up to $\frac{1}{500}$ of a degree. Insulation of this cylinder is made as perfect as possible, in order to prevent loss of heat by radiation.

The experiments made, are completed in as short a time as possible ; the actual rise in temperature of the water is never allowed to exceed a few degrees, and great care is taken to distribute the heat generated uniformly through the water, by means of mechanical stirrers, which are kept constantly in motion during the progress of the experiment.

Of course, the weight of all parts of the apparatus, as well as that of the water, must be very carefully ascertained. Furthermore, allowance must be made for the specific heat of the metal, of which the apparatus is constructed.

If, for instance, the vessel is made of platinum, which has a specific heat of 0.032, and if it has a weight of 180.0 grammes, then:

$$180.0 \times 0.032 = 5.760,$$

which amount must be added to the weight of the water contained in the calorimeter, for this weight of platinum is equivalent to, i.e., has the same calorific value, as 5.760 grammes of water.

Lavoisier was probably the first one to study thermo-chemical phenomena from a theoretical point of view; he recognized the principle, that, in the formation of a compound from its elements, the same amount of heat is set free as is required to decompose this compound. In 1840, G. H. Hess announced the important law of constant heat-summation, viz.: "the initial and final stages alone determine the development of heat in chemical processes."

Laws of Thermochemistry.—The following are the three fundamental laws of thermochemistry as formulated by Berthelot:

I. The amount of heat set free in any chemical reaction is a measure of the total work, both chemical and physical, accomplished in the reaction.

II. Whenever a system of bodies undergoes physical or chemical changes capable of bringing it to a new state, without producing any mechanical effect exterior to the system, the amount of heat set free or absorbed in these changes, depends only on the initial and final states of the system, and is independent of the nature or order of the intermediate states.

III. Every chemical change which is effected in a system without the aid of outside energy, tends to the production of that body or system of bodies, the formation of which, evolves the maximum heat.

These principles permit the determination of thermal values of reactions, which cannot be directly measured.

In 1853, Julius Thomsen first applied the results of the mechanical theory of heat, to thermo-chemistry.

The principal work thus far done in thermochemistry, has resulted in the accumulation of a very great number of observations concerning the heat of formation of substances.*

In making these determinations on the heat of formation of compounds, the molecules of the elements have been chosen as the starting point. However, as for the most part the molecules of elements are combinations of atoms, and as in the formation of molecules from these atoms chemical energy must have come into play, the problem of ascertaining the heat of formation of compounds is not a simple one.

For, before the molecules of compounds can be formed, the atoms which make up the molecules of the elements engaged in the reaction, must be separated from one another. This requires energy, and therefore the heat of formation of a compound merely expresses the *difference* in energy (heat), between the amount required to separate the atoms of the elementary molecules, and the amount of energy (heat) evolved or absorbed in the formation of the new compound.

If the latter value is greater than the former, and this is generally the case, the heat of formation of a compound is a plus (+) value; if the energy (heat), evolved on the formation of a compound is less than the energy required to separate the atoms of the original molecules, then the heat of formation of that compound is a minus (—) value.

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* For tables of these data see the "Annuaire," published by the Bureau des Longitudes in Paris.

Also, Ostwald: Outlines of General Chemistry; and, Muir and Wilson: The Outlines of Thermal Chemistry.

Exothermous and Endothermous Compounds.—Those substances whose formation is attended by the evolution of energy (heat), are called *exothermous* compounds, while those substances whose formation is attended by an absorption of energy (heat), are called *endothermous* compounds.

The latter as a rule, are very unstable substances, for the tendency of all matter is to assume that state of equilibrium, which is most stable under existing conditions, and as already stated, in every chemical reaction, the tendency is to form those products whose formation gives rise to the evolution of the greatest quantity of heat.

The Language of Thermochemistry.—The ordinary chemical formulæ and equations express relations by mass, that is to say, in addition to showing the substance or substances concerned in a reaction, and the substance or substances produced, they show the amounts of the different factors involved.

Thus, the equation.

$$\mathrm{Na} + \mathrm{Cl} = \mathrm{NaCl}$$

not only expresses the fact, that the element sodium combines with the element chlorine to form the compound sodium chloride, but it also shows, that this reaction takes place between 23 parts by weight of sodium and 35.5 parts by weight of chlorine, and that $23 + 35.5 = 58.5$ parts by weight of sodium chloride are produced.

If, in addition to this, it be desired to indicate the amount of energy involved in a chemical reaction, for instance, in the reaction above given, the equation must be extended, so as to show the amount of heat involved, for chemical energy, it will be remembered, is here to be measured in thermal units.

By experiment it has been found, that the formation of NaCl from Na and Cl is accompanied by the evolution of

97600 gramme-calories, and in order to indicate this fact, the equation above given, viz.:

$$\text{Na} + \text{Cl} = \text{NaCl}$$

must be written as follows:

$$\text{Na} + \text{Cl} = \text{NaCl} + 97{,}600 \text{ g. c.}$$

This shows, that 23.0 grammes of Na and 35.5 grammes of Cl, together contain the same amount of energy as 58.5 grammes of NaCl plus 97,600 g. c.

This equation can be variously transformed.

Thus for instance:

$$(1)\ \text{NaCl} = \text{Na} + \text{Cl} - 97{,}600 \text{ g. c.}$$

which means, that in order to decompose NaCl into its constituents, 97,600 gramme-calories must be furnished.

Or, again :

$$(2)\ \text{Na} + \text{Cl} - \text{NaCl} = 97{,}600 \text{ g. c.}$$

This shows, that 97,600 gramme-calories is the difference in energy between Na plus Cl and NaCl.

To furnish another illustration of thermochemical expression:

$$\text{H} + \text{I} = \text{HI} - 6100 \text{ g. c.}$$

This shows, that the formation of hydro-iodic acid from iodine (solid), and from hydrogen, is attended by an absorption of heat, equivalent to 6100 gramme-calories.

By transforming above equation algebraically:

$$\text{HI} = \text{H} + \text{I} + 6100 \text{ g. c.}$$

From this it will be seen, that a breaking up of HI into its constituents H and I, is accompanied by an evolution of 6100 gramme-calories.

Most of the data expressing the energy of chemical reactions, have been obtained at, or are referred to, a normal temperature of 18° C. The mass-amounts of the substances involved in these reactions always correspond to the atomic or the molecular masses of the substances, expressed in grammes. The thermal unit employed is either the gramme-calorie as here used, or a value 1000 times as great, and termed the kilogramme-calorie.

The condition in which the substances exist, i.e. whether in the solid, the liquid, or the gaseous state, exercises an important bearing on the amount of energy associated with the same. Very frequently the reactions studied, take place in large quantities of water. This, within certain limits, does not affect the thermal relations, and the symbol Aq (aqua) is used to indicate water when it thus exists as a passive factor in a reaction.

Energy-equations.—The examples thus far given, illustrate the heat of formation of an exothermous and of an endothermous compound. Very often however, it is not possible to measure the thermo-chemical values of a given reaction directly, and in these instances, use is made of the fundamental principle, that the initial and final stages alone, determine the amount of heat of a chemical reaction.

All that is required, is to execute and to measure any two reactions in which the initial and the final substances take part, and to devise a series of equations by means of which all intermediate reactions can be eliminated.

As already stated, the heat of formation of a compound is merely the difference between the chemical energy of the compound formed, and that of the elements which form it.

$$\text{Na} + \text{Cl} = \text{NaCl} + 97{,}600 \text{ g. c.},$$

signifies that the heat of formation of sodium chloride is 97,600 gramme-calories, as before stated.

Therefore, 97,600 g. c. is the loss of energy experienced by the sodium and the chlorine in forming the compound sodium chloride.

The absolute magnitudes of the quantities of energy involved, are unknown. If the energy of the elements be taken as zero, and the quantities of energy be figured therefrom, then, if: $Na = 0$ and $Cl = 0$, the equation:

$$Na + Cl = NaCl + 97{,}600 \text{ g. c.}$$

can be written:

$$0 + 0 = NaCl + 97{,}600 \text{ g. c.}$$

and this corresponds to:

$$-97{,}600 \text{ g. c.} = NaCl.$$

From this it follows, that in energy-equations, the heats of formation of compounds with their *signs changed*, can be substituted for the formulæ of these compounds, and this principle is frequently used in thermochemical calculations.

The following selected examples will illustrate the solving of thermochemical problems.

Example I.—Calculate the heat of formation of carbon monoxide. The data obtained by experiment, are:

$$C + 2O = CO_2 + 97{,}000 \text{ g. c.} \quad (A)$$
$$CO + O = CO_2 + 68{,}000 \text{ g. c.} \quad (B)$$

Subtracting *B* from *A*:

$$C + 2O - CO - O = 29{,}000 \text{ g. c.}$$

Hence:

$$C + O = CO + 29{,}000 \text{ g. c.}$$

The heat of formation of CO is therefore 29,000 g. c.

Example II.—Determine the heat of formation of hydrobromic acid, from the following data;

A. $(KBr + Aq) + \frac{1}{2}Cl_2 = (KCl + Aq) + (\frac{1}{2}Br_2 + Aq)$ 11,478 g. c.
B. $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 + Aq = (HCl + Aq)$ 39,315 g. c.
C. $(KOH + Aq) + (HCl + Aq) = (KCl + Aq)$ 13,750 g. c.
D. $(KOH + Aq) + (HBr + Aq) = (KBr + Aq)$ 13,750 g. c.
E. $\frac{1}{2}Br_2 + Aq = (\frac{1}{2}Br_2 + Aq)$ 539 g. c.
F. $HBr + Aq = (HBr + Aq)$ 19,940 g. c.

From *A*:

1. $(KCl + Aq) = 11{,}478 + (KBr + Aq) - (\frac{1}{2}Br_2 + Aq)$.

From *E*:

$$(\tfrac{1}{2}Br_2 + Aq) = 539.$$

Hence:

2. $(KCl + Aq) = 10{,}939 + (KBr + Aq)$.

From *C*:

$$(KCl + Aq) = 13{,}750 + (KOH + Aq) + (HCl + Aq).$$

From *B*:

$$(HCl + Aq) = 39{,}315.$$

Hence:

3. $(KCl + Aq) = 53{,}065 + (KOH + Aq)$.

Placing the second members of equations No. 2 and No. 3 equal to each other:

$$10{,}939 + (KBr + Aq) = 53{,}065 + (KOH + Aq).$$

4. $(KBr + Aq) = 42{,}126 + (KOH + Aq)$.

From *D*:

5. $(KBr + Aq) = 13{,}750 + (KOH + Aq) + (HBr + Aq)$.

Placing the second members of equations No. 4 and No. 5 equal to each other:

$$42{,}126 + (KOH + Aq) = 13{,}750 + (KOH + Aq) + (HBr + Aq).$$

Hence:

6. (HBr + Aq) = 28,376.

In *F.* the heat of solution of HBr is given = 19,940.
Hence:

$$H + Br = HBr = 28,376 - 19,940,$$

and the heat of formation of HBr is therefore equal to 8436 gramme-calories.

CHAPTER XIII.

PHOTO-CHEMISTRY.

Introductory.—Light, one form taken by the radiant energy emanating from the sun, is a powerful agent in effecting chemical changes.

It can induce chemical union between substances, it can cause the decomposition of chemical compounds, and, in certain instances it can produce important alterations in the physical, as well as in the chemical, properties of the matter subjected to its influence.

Chemical Union.—A mixture of hydrogen and chlorine, if kept in the dark, will remain practically unchanged. On exposure to diffused light chemical combination will gradually ensue, but, if a mixture of these gases be exposed to direct sunlight their union is accomplished instantaneously and with great violence ; an explosion usually accompanying the reaction.

Chemical Decomposition.—Chlorine gas can be kept unchanged in aqueous solution for a long time, provided it be carefully guarded from the light. Exposed to its influence the water is partially decomposed, hydrochloric acid is formed and oxygen liberated.

Potassium iodide is decomposed by sunlight, iodine being set free. Concentrated nitric acid suffers partial decomposition if acted on by light; some of the oxides of nitrogen are formed, and these impart a yellow or brown coloration to the otherwise colorless acid.

Many organic coloring matters fade and bleach, because light promotes the affinity of the atmospheric oxygen for two of their principal constituents, carbon and hydrogen.

Most silver salts are blackened by the action of light, and it is on this action of light upon some of the silver salts, that the art of photography is based. A plate of glass, or of some other transparent material, is coated with iodide of silver,—one of the silver compounds most sensitive to light. The plate thus prepared is placed in a camera, and the image of the object which is to be photographed is allowed to fall upon it. The plate is then immersed in a solution of ferrous sulphate or of some other reducing agent, and thereby the iodide of silver, which has been acted upon by the light, is more or less blackened and the picture is thus developed.

In order to fix the picture and avoid any further action of the light on the plate, the iodide of silver which remains is removed by washing with a solution of potassium cyanide, or of sodium thiosulphate, commonly termed, sodium hyposulphite. The plate thus prepared constitutes the negative. On this of course, those parts of the image which in the object pictured were brightest, appear most dark, for from them came the greatest amount of light, and this light affected the iodide of silver directly in proportion to its intensity.

To print pictures from a negative, the latter is placed on a surface, generally paper, coated with chloride of silver, and then light is allowed to fall upon it. The rays of light of course pass most readily through the undarkened portions of the negative, and thus produce in the film of chloride of silver a darkening, a distribution of light and shade, which is exactly the reverse of that existing on the negative. The picture thus formed—the positive—is then fixed, made permanent, by the use of proper reagents, and the photograph is finished.

But most important of all, must be counted the transformation of radiant energy into chemical energy, through the agency of plants. Plants absorb carbon dioxide from the air, and under the influence of sunlight this compound is decomposed into carbon and oxygen; the former is stored in the plant, the latter is returned to the atmosphere.

That green plants, in sunlight, will purify air containing carbon dioxide, was noticed by Priestley as early as 1772. The full importance of this process in the economy of Nature was however pointed out only by Justus von Liebig, almost seventy years later.

Physical Changes.—Among the most frequently cited phenomena of this description is the transformation of the common, colorless variety of phosphorus into its red amorphous modification; this change of outward form and color is moreover accompanied by very great alterations in the chemical properties of the substance.

The influence which light exercises on the crystallization of inverted sucrose solutions, has been made the subject of study by the author. Three solutions of invert-sugar were prepared from chemically pure sucrose; the first contained 90.9%, the second 80.6% and the third 58.0% of invert-sugar.

These solutions were placed into twenty-four glass flasks and these were divided into four groups A, B, C, D, of six flasks each. Each of these groups contained the following samples:

90.9%	invert-	sugar.	Sol.:	slightly acid
90.9 “	“	“	“	neutralized
80.6 “	“	“	“	slightly acid
80.6 “	“	“	“	neutralized
58.0 “	“	“	“	slightly acid
58.0 “	“	“	“	neutralized.

Group A. was exposed to direct sunlight, group B. to diffused daylight, group C. to the rays of an electric arc-light, group D. was kept in darkness.

As a full account of the interesting relations brought out in this investigation would here not be in place, mention shall only be made of the fact, that crystallization—by which is meant transformation of the *entire* fluid contents of the flasks into the solid state,—was effected in five of the flasks exposed to direct sunlight, before a single one of the other series attained to this condition.

The series exposed to diffused daylight was the next to experience this transformation, and this, while the solutions which were kept in darkness, for the greater part still retained their fluidity.

Mode of Action.—The chemical action of light depends upon its absorption—this has been proved by experiment.

As a substance does not absorb all wave-lengths of light alike, the chemical effects which the different color-rays exercise on a body are not identical. It has been determined that the chemical effect of light is dependent upon the color of the light and upon the nature of the body on which it acts.

The short wave-lengths of light, the violet rays, are generally held to be the most powerful in inducing chemical changes. However, in the work performed in plants—the decomposition of carbon dioxide into its constituents, the red and the yellow rays are the principal agents, and in fact, all rays of light are capable of producing chemical effects.

An hypothesis advanced to explain the chemical action of light holds, that the vibrations of the luminiferous ether excite in the substance acted upon, corresponding vibrations, that is to say, vibrations of the same period as those of the ether. The molecules which thus receive this supply of energy, are thrown into commotion, and the atoms, constituting these molecules, will tend to assume different positions. If this disturbance results in the production of more stable molecular systems, for instance, in the decomposition of a compound into its constituents, some of the radiant energy absorbed may be used for this purpose and remain in the system as bound energy.

Measurement of the Chemical Activity of Light.—Attempts to effect such measurement, have been made in various ways. Senebier prepared a number of papers coated with argentic chloride, upon which light of a known intensity was allowed to act for a certain time. The amount of blackening which these papers experienced, depended of course upon the intensity of the light acting upon them, and upon the time of their exposure. In this manner, a sort of scale was obtained, which was of value for comparative measurements.

Bunsen and Roscoe perfected a method, originally indicated by Draper, in which the formation of hydrogen chloride by the action of light, is made the basis of operations. Hydrogen and chlorine gases, in the proportion of their chemical equivalents are introduced into a thin glass bulb, the lower half of which is blackened, and in which water has been placed. This bulb is in connection with a measuring tube, which terminates in another vessel, also containing water.

The light falling upon the mixture of hydrogen and chlorine, causes their chemical union, forming hydrochloric acid gas, and this is at once absorbed by the water.

The consequent diminution in volume causes the water in the measuring tube to move towards the bulb wherein the hydrochloric acid was formed. The amount of water thus moved, is ascertained from the scale on the tube, and this affords a measure of the activity of the light, which has induced the chemical union of the hydrogen and the chlorine.

CHAPTER XIV.

ELECTRO-CHEMISTRY.

Introductory.—The proof that chemical energy can be transformed into electrical energy, is easily given.

Pure zinc and pure platinum are not attacked by dilute sulphuric acid, whether these metals are immersed singly, or together, only provided, that they do not come into contact with each other. The instant however, that contact is established between them, either by placing them together, or by connecting them by some piece of metal, the zinc will be attacked by the sulphuric acid and will commence to dissolve, while bubbles of a gas will appear on the surface of the platinum.

The connecting wire will at the same time be found to have become endowed with certain properties which it did not possess before it served to connect the pieces of metal, and which properties it loses, the instant that its connection with one or both of the metals is broken, or, when one of the latter is removed from the liquid.

This clearly demonstrates the fact, that the energy set free by action of the sulphuric acid on the zinc, has become transformed into a form of energy which is capable of passing from the place of its liberation, and is capable of doing work elsewhere in its course, in the so-called electrical circuit, which then becomes the seat of the electrical current.

The existence of this electric current can be shown to be due entirely and only to the chemical action between the acid and the metal; the amount of electricity generated, stands in direct relation to the amounts of chemicals, zinc and sulphuric acid, involved in the process.

Electrical energy must be regarded as the product of two factors, quantity and tension. This latter is also termed electro-motive force, or potential. The electro-motive force in its more general sense, is the force which tends to move the electricity from one point of the circuit to another; its more specific meaning will be defined later.

The electro-motive force, in establishing and maintaining an electrical current, has to overcome a certain amount of frictional resistance; the work which the electro-motive force does in overcoming this frictional resistance, appears as heat.

Electrolysis.—If the electric current is made to pass through a certain class of conductors, solutions of acids, salts, etc., certain chemical changes take place in the system, simultaneous with the passing of this current, and the energy which these chemical changes represent, forms the remaining part of the work done by the electro-motive force in establishing and maintaining the electrical circuit.

Chemical decomposition brought about by a current of electricity is termed, electrolysis.

The substance decomposed, is called an electrolyte, and the constituents produced, are known as ions. The poles are called electrodes. The metals of salts, metallic radicals, and the hydrogen of acids, are always liberated at the negative electrode (cathode), which is that electrode in connection with the metal most strongly attacked by the acid; these ions are termed positive ions, or cathions. The acid radicals, oxygen, chlorine, bromine, iodine, the group hydroxyl, etc., are set free at the positive electrode (anode), and are termed negative ions, or anions.

Only certain classes of compounds are capable of serving as electrolytes.

The Ion Theory.—From certain phenomena it appears probable, that it is not the electric current which effects the decomposition of compounds into ions, but that these ions pre-exist in all solutions which can serve to conduct an electric current.

This view was first suggested by Williamson (1851) and independently by Clausius, six years later. Clausius assumed, that the presence of only a very few free ions in a solution was necessary in order to make such a solution a conductor of electricity.

The atoms of the base and the acid, constituting the salt in solution, were not supposed to be firmly united to one another, but were, in virtue of molecular encounters, supposed to readily enter into new combinations. Thus, molecule I, formed of one atom of base B and one atom of acid radical A, and molecule II, also formed of one atom of the same base B and the same acid radical A, would both be readily decomposed, and give rise to the formation of two new molecules of the same compound. One of these newly-formed molecules would consist of base B, of the original molecule I in combination with acid radical A of original molecule II, and the other newly-formed molecule would consist of base B of the original molecule II combined with the acid radical A, of original molecule I.

While these exchanges were going on, the electricity was supposed to make use of some of these momentarily free atoms for its transportation to the electrodes.

Electrolytic Dissociation.—However, in 1887, this theory, which failed to account for many phenomena, was replaced by Arrhenius by a theory which is now known as, the theory of electrolytic dissociation.

This investigator reached the conclusion, that in electrolytic solutions, for instance in aqueous solutions of strong acids and bases, these substances are either wholly, or at least in great part, dissociated, that is to say, that their constituents are present in the form of free ions. In dilute solutions the dissociation of a substance into free ions, is most perfect. For the laws governing this dissociation are the same as those which control gaseous dissociation, and the dissociation of gases increases with a decrease of pressure. But in solution, we have the osmotic pressure analogous to gaseous pressure, and the osmotic pressure of a solution is decreased as the concentration of the solution is lessened, therefore, dilution decreases the osmotic pressure and correspondingly encourages dissociation into ions.

Attention must be called to the fact, that an ion of an element does not correspond to a free atom of that element.

For instance, if a solution of sodium chloride were used as an electrolyte, the ions would of course consist of sodium and of chlorine. But the sodium ions and the chlorine ions, as long as they exist as ions, that is to say, as long as they are charged with electricity, do not behave like the ordinary free atoms of sodium and of chlorine. The sodium ion, for instance, will not decompose water, while, as is well known, sodium not electrically charged will do this most energetically; likewise, the ion chlorine behaves differently from an ordinary free atom of chlorine. But when the charges of electricity which the ions bear, have been discharged at the respective electrodes, the elements resume their customary properties and functions. Ions may be either atoms of elements, or groups of atoms.

The anions carry negative, the cathions bear positive electricity. These ions of course move towards opposite electrodes; those charged with positive electricity move towards the negative electrode, and those charged with negative electricity travel to the positive electrode, and there discharge their electricity. Thus, in decomposing a solution of sulphate of copper, the copper atoms, after giving up their charge of electricity, are precipitated as metallic copper, while the SO_4 radical decomposes the water in which the reaction takes place, forming sulphuric acid and liberating oxygen gas.

An interesting point to be mentioned in this connection is the fact, that chemical reactions for certain substances can be obtained only, when the substances tested for, can appear, on electrolysis, as free ions, and not, when these substances occur as constituents of complex ions.

Thus, for instance, chlorine is generally tested for by nitrate of silver. But while this test is a very satisfactory one for free chlorine, for chlorine when existing in the form of hydrochloric acid and in the form of numerous metallic chlorides, it will not answer for the detection of chlorine when in the form of potassium chlorate. Careful examination shows, that this test for chlorine can be obtained only in such of its compounds, which, when subjected to electrolysis, yield the chlorine as a free ion.

The tendency of the ions of an electrolyzed solution to recombine chemically, gives rise to an electro-motive force, which is called the electro-motive force of polarization, and which has been regarded as offering a means to measure the chemical affinity of the ions.

Electrical Units.—Whenever an electric current is established in a closed circuit, and performs work at different points of its path, any and all chemical changes which are induced, will be found to be the exact chemical equivalents of each other. These quantitative relations were first enunciated by Faraday, and are expressed in his laws. Before however passing on to a consideration of these relations, the system of units employed for the measurement of electrical energy requires mention.

In the centimetre-gramme-second system, generally referred to as the C. G. S. system of units, the centimetre is adopted as the unit of length, the gramme as the unit of mass, and the second as the unit of time.

From these fundamental units there are derived the C. G. S., or as they are sometimes called, the "absolute" units of velocity, acceleration, force, work, energy, and, heat; they are as follows:

UNIT OF VELOCITY: the velocity of one centimetre per second.

UNIT OF ACCELERATION: an acceleration of one centimetre-per-second per second.

UNIT OF FORCE: that force which acting for one second on a mass of one gramme, imparts to it a velocity of one centimetre per second. It is named the Dyne.

UNIT OF WORK: the work done in moving a body one centimetre against the force of one Dyne. It is named the Erg.

UNIT OF ENERGY: the Erg as above defined, for the energy of a system is measured by the work it can accomplish.

UNIT OF HEAT: the amount of heat required to raise the temperature of one gramme-mass of water from 0° to 1° C. It is termed the gramme-calorie.

Two systems of electrical units are derived from these fundamental units: the electro-static, and the electro-magnetic units. The *practical* units employed in the measurement of electrical quantities follow; they are derived from the electro-magnetic units.

The Ohm = unit of resistance.

(10^9 C. G. S. units of resistance.)

It is the resistance offered by a column of mercury 106.28 c.m. long and 1 sq. mm. in section at 0° C.

The Volt = unit of electromotive force.

(10^8 C. G. S. units of electro-motive force.)

The electro-motive force of a Daniell cell is 1.079 volts.

The Coulomb = unit of quantity.

(10^{-1} C. G. S. units of quantity.)

It is the quantity of electricity which in one second flows through the section of a conductor between the ends of which there is an electro-motive force of 1 Volt, and the resistance of which is 1 Ohm.

The Ampère = unit of current-strength.

(10^{-1} C. G. S. units of current.)

It is the current produced by 1 Volt through 1 Ohm, i.e., 1 Coulomb per second, is 1 Ampère.

The Watt = unit of power, i.e., the rate of doing work.

(10^7 C. G. S. units of power.)

It is the power conveyed by a current of 1 Ampère in 1 second through a difference of potential of 1 Volt.

The Farad = unit of capacity.

(10^{-9} C. G. S. units of capacity.)

It is the capacity of a condenser that will be raised to a potential of one Volt by a charge of one Coulomb. (As a condenser of this capacity is too large to be constructed, the Micro-farad = 0.000001 Farad is adopted as the working unit of electrical capacity.)

The Joule = unit of work or heat.

(10^7 C. G. S. units of work.)

It is the mechanical equivalent of the heat generated per second by a current of 1 Ampère flowing through a resistance of 1 Ohm, i. e. the heat generated by 1 Watt.

To indicate quantities a million times as great as those here given, the word *mega-* is prefixed to the term; in order to denote quantities a million times as small, the prefix *micro-* is employed; while quantities one thousand times as small are designated by the prefix *milli-*.

The system of index notation, as used above in expressing values in the C. G. S. system, has been adopted for the sake of convenience and in order to economize space. Only the significant figures of a quantity are written down, the ciphers are indicated by an index written above.

Thus:

$$100 = 10 \times 10 = 10^2$$
$$1000 = 10 \times 10 \times 10 = 10^3$$
$$10000 = 10 \times 10 \times 10 \times 10 = 10^4$$

and thus 90,000 can be written: as 9×10^4

Decimals have negative indices. Thus 0.000128 is expressed by: 128×10^{-6} as it is equal to $128 \times .000001$.

Quantitative Relations.—The following formulæ express some of the relations existing between electrical units.

Let,

C denote Ampère,
E “ Volt,
R “ Ohm,
W “ Watt,
H “ Heat-work,
Q “ Quantity of electricity,
t “ time,

Then,

$$C = \frac{E}{R} \qquad \text{(Ohm's Law.)}$$

$$E = C \times R$$

$$R = \frac{E}{C}$$

$$W = C \times E$$

$$W = \frac{E^2}{R}$$

$$W = C^2 R$$

$$H = C^2 R t \quad \text{(Joule's Law.)}$$

$$H = QE$$

$$Q = Ct$$

The amount of the ion set free in a given time, at an electrode, is dependent upon the strength of the current, and is directly proportional to it. This is one of Faraday's electrolytic laws.

One Coulomb of electricity, in passing through water, liberates an amount of hydrogen which has been variously stated to be *:

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* S. P. Thompson: Elementary Lessons in Electricity and Magnetism. 1892.

0.000010352	gramme,	Lord Rayleigh
0.000010354	"	Kohlrausch
0.000010415	"	Mascart

This quantity is termed the *electro-chemical equivalent* of hydrogen.

The electro-chemical equivalent of any element is obtained by dividing the atomic mass of the element by its valence, and then multiplying the resulting quotient by 0.000010352.

Thus, the electro-chemical equivalents, (expressed in gramme per Coulomb), of a few of the elements are as follows:

Silver	$\frac{108}{\text{I}} \times .000010352 = 0.0011180$
Copper in cupric compounds	$\frac{63.6}{\text{II}} \times .000010352 = 0.0003292$
Copper in cuprous compounds	$\frac{63.6}{\text{I}} \times .000010352 = 0.0006584$
Zinc	$\frac{65.3}{\text{II}} \times .000010352 = 0.0003379$
Oxygen	$\frac{16}{\text{II}} \times .000010352 = 0.0000828$

The actual weight in grammes of any ion liberated by electrolysis is obtained by the formula:

$$w = zct,$$

where, w = weight in grammes,
z = the electro-chemical equivalent of the ion,
c = strength of current in Ampères,
t = time in seconds during which the current flows.

This principle has been practically applied by Edison in measuring the quantities of electricity supplied to stations from central electric plants. A solution of cupric sulphate is electrolyzed between two copper electrodes. The anode will be dissolved by the current, while the equivalent amount of copper will be deposited on the cathode. Therefore, if one of these electrodes is weighed before and after the passage of the electric current, the quantity of electricity which has passed can be readily calculated.

If a metal which has been deposited by an electric current is made to undergo combustion, or is dissolved in acid, its potential energy will be given up in the form of heat, and the equivalent amount of work can be easily calculated, provided, that the mechanical equivalent of heat has been ascertained.

As stated by Thompson: "The electro-motive force of any chemical reaction is equal to the product of the electro-chemical equivalent of the separated ion into its heat of combination, expressed in dynamical units." Embodying this in a formula, and exemplifying by a problem*:

$$e = zHJ$$

where, z = absolute electro-chemical equivalent, in grammes, of the ion. †

H = number of heat-units evolved by 1.0 gramme of the substance on entering into the combination considered.

J = Joule's equivalent.

Example: Find the electro-motive force of hydrogen tending to unite with oxygen.

For hydrogen, $z = 0.00010352$,

$H = 34{,}000$ gramme-calories,

$J = 42 \times 10^6$

$.00010352 \times 34{,}000 \times 42 \times 10^6 = 1.47 \times 10^8$ absolute units of electro-motive force. As 10^8 absolute units of electro-motive force are equivalent to one Volt, the value found corresponds to 1.47 Volts.

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[*] S. P. Thompson, loc. cit. p. 389.

[†] The *absolute* electro-chemical equivalents are ten times as great as the values previously given for the electro-chemical equivalents, for the Coulomb is 0.1 of the C. G. S. unit of quantity.

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